REMEDIATION OF CHROMIUM(VI) IN THE VADOSE ZONE: STOICHIOMETRY AND KINETICS OF CHROMIUM(VI) REDUCTION BY SULFUR DIOXIDE

A Thesis

by

MIN AHN

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

August 2003

Major Subject: Civil Engineering

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Approved as to style and content by:

Bill Batchelor (Chair of Committee)	Bruce E. Herbert (Member)
Robin L. Autenrieth (Member)	
Paul N. Roschke (Head of Department)	

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ABSTRACT

Remediation of Chromium(VI) in the Vadose Zone: Stoichiometry and Kinetics of Chromium(VI) Reduction by Sulfur Dioxide. (August 2003)

Min Ahn, B.S., Seoul National University

Chair of Advisory Committee: Dr. Bill Batchelor

Immobilization and detoxification of chromium in the vadose zone is made possible by the existence of an effective reductant, SO_2, that exists in a gaseous form at room temperature. Experimental studies were designed to characterize stoichiometry and kinetics of chromium reduction both in aqueous solutions at pH values near neutrality and in soil.

First, batch experiments and elemental analyses were conducted to characterize the stoichiometry and kinetics of Cr(VI) reduction in water. The stoichiometric ratio of S(IV) removed to Cr(VI) removed ranged between 1.6 and 1.8. The overall reaction is believed to be the result of a linear combination of two reactions in which dithionate is an intermediate and sulfate is the stable oxidized product. The reaction was also rapid, with the half-time of about 45 minutes at pH 6 and about 16 hours at pH 7. A two-step kinetic model was developed to describe changes in concentrations of Cr(VI), S(IV), and S(V). Nonlinear regression was applied to obtain the kinetic parameters. The rate of reaction was assumed to be second-order with respect to [Cr(VI)] and first-order with respect to [S(IV)], and [S(V)]. The values for the rate coefficient for the first reaction

(k_1) were found to be 4.5 (± 10%), 0.25 (± 9.4%) ($mM^{-2}h^{-1}$) at pH 6 and 7, respectively. The values of the rate coefficient for the second reaction (k_2) were 25 (± 29%), 1.1 (± 30%) ($mM^{-2}h^{-1}$) at pH 6 and 7, respectively. The reaction rate decreased as pH increased. Experiments showed that the rate at pH 7 was lower than that at pH 6 by one order of magnitude.

Second, batch experiments and elemental analyses were conducted to characterize the stoichiometry and kinetics of Cr(VI) reduction in soil. The stoichiometric ratio of S(IV) removed to Cr(VI) removed was almost 2, which is slightly higher than that for the reaction in water. This higher value may be due to S(IV) oxidation by soil-derived Fe(III). The reaction was rapid, with the half-time less than 2 minutes, which is faster than in water. The rate coefficients, k_1 and k_2, were 22 (± 41%) and 13 (± 77%) ($M^{-2}h^{-1}$), respectively.

To my wife, Jeong-Soon, and babies, Yerim and Moojin

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In particular, I would like to thank Dr. Woojin Lee for his support and encouragement. Thanks to my lab colleagues, Saebom Ko, Ahmed Abdel-Wahab, Jeong-Yoon Choi and Bangmi Jung, for their opinions in my research as well as their friendship.

I would like to express my appreciation and love to my mother and lovely wife, Jeong-Soon, for their endless love, support and encouragement. I can't imagine this completion without them. Finally, I would like to thank my God for being always with me and bringing me strength and patience.

TABLE OF CONTENTS

LIST OF FIGURES

Page

LIST OF TABLES

CHAPTER I

INTRODUCTION

Chromium is an important metal used in numerous industrial activities, including electric-power production, electroplating, leather tanning, pulp production, and ore and petroleum refining, and those activities produce significant quantities of chromium wastes (*1*). Chromium contamination in soils and water is caused by leakage, unsuitable storage, or improper disposal practices of chromium wastes and it is reported at 43 % of the hazardous waste sites on the National Priorities List in the United States (*2*).

Chromium is present in the environment in several different forms and normally found in the +III and +VI oxidation states (*3*). Cr(III) is considered to be less toxic than Cr(VI), and even essential to human health in microgram quantities (*4, 5*). Meanwhile, Cr(VI) is a carcinogen, an irritant, and it is corrosive. It can be absorbed by ingestion, through the skin, and by inhalation. Cr(VI) can be reduced to Cr(III) by numerous reductants including Fe(II), organic matter and reduced sulfur compounds (*6, 7*).

Cr(III) is environmentally preferred over Cr(VI), because it is relatively immobile and less toxic. Immobilization of chromium is caused by precipitation of Cr(III) in the form of hydroxide solids or by sorption onto soils. Re-oxidation of Cr(III) to Cr(VI) is generally not observed in soils, unless there are high levels of manganese (*6, 8*).

This thesis follows the style of the *Environmental Science and Technology*.

Therefore, reduction of Cr(VI) to Cr(III) is an effective approach to remediation by reducing risk to human health and the environment through reduction in toxicity and mobility.

The major route of exposure to chromium at sites is transport through groundwater, because of the mobility of Cr(VI) in soils. At most sites, chromium has been released near the surface and has traveled through a vadose zone before contaminating the groundwater. Limiting movement of chromium through the vadose zone provides an opportunity to protect groundwater and it could be accomplished by reducing Cr(VI) to Cr(III). This would further reduce risk by also reducing toxicity. The deeper the vadose zone is, the greater the potential opportunity to protect groundwater.

Immobilization and detoxification of chromium in the vadose zone is made possible by the existence of an effective reductant, SO_2, that exists in a gaseous form at room temperature. A gas-phase reductant can be effectively transported through the vadose zone in combinations of extraction and injection wells similar to those used for soil vapor extraction of volatile organics. Combination of the reducing power of SO_2 and low cost contacting equipment developed for soil vapor extraction provides the opportunity to develop low cost, effective remedial technologies for chromium in contaminated vadose zones.

The goal of the research is to develop fundamental information on the reduction of Cr(VI) in soils by sulfur dioxide that can be used to develop remedial technologies. This goal will be achieved through laboratory experiments as described by the following two research objectives. Objective 1 is to develop analytical and experimental procedures.

Experimental equipment and procedures needed to carry out experiments will be developed. Successful completion of objective 1 will provide the basis for confidence in the experimental results of the research. Objective 1 will be fully achieved when reproducible results are obtained and analytical procedures meet the criteria of QA/QC plan for this research. Objective 2 is to characterize stoichiometry and kinetics of chromium reduction. This objective will be pursued through work on two sub-objectives. The first sub-objective is to quantify stoichiometry and kinetics of Cr(VI) reduction by dissolved SO_2 in aqueous solution at pH values near neutrality. Despite the widespread use of this process at low pH for wastewater treatment, there is very little quantitative information in the literature on the process at values of pH near pH 7 that are expected in soils. Information on the behavior of this reaction in aqueous solution will aid design and interpretation of results in soil systems. The second sub-objective is to obtain data on stoichiometry and kinetics of reduction of Cr(VI) on soils by gaseous SO_2. The effect of water content will be evaluated. These results will be used to predict and optimize effectiveness of remedial technologies.

CHAPTER II

BACKGROUND

2.1. In Situ Gaseous Reduction

In Situ Gaseous Reduction (ISGR) is a treatment method that can be applied to soils that are contaminated with redox-sensitive metals, such as chromium and uranium (*9*). Hexavalent chromium is quite mobile and can be easily carried by waters penetrating the unsaturated zone. However, reduction to the trivalent state would greatly reduce the mobility of chromium. Reduction and immobilization of hexavalent chromium in soils can potentially be achieved through treatment with an effective reductant, SO_2.

ISGR uses a network of injection and extraction wells within the contaminant plume in the subsurface (figure 1) (*9*). Treatment is accomplished by injecting the gas mixture into a central well and extracting gases by applying a vacuum in wells located at the plume boundary. Monitoring the breakthrough of the gas at the extraction wells is practiced over time for the assessment of treatment progress. This is also accomplished by comparing Cr(VI) concentrations in core samples before and after treatment.

The baseline technology for soil remediation is excavation, followed by treatment and disposal. This technology has a limitation when a contaminant is present at greater depths, but ISGR can overcome this limitation. Furthermore, ISGR has several other advantages: reduced exposure of workers to contaminated media, minimized disturbance of environment, minimized waste generation, and potential cost savings. The laboratory treatability test with H_2S gas mixtures for reduction of Cr(VI) showed that greater than

99% of the Cr(VI) present in the contaminated sediments was reduced and performance of the ISGR field demonstration at White Sands Missile Range, New Mexico, indicated that 70% of the Cr(VI) present at the site was reduced to Cr(III) during the demonstration, with final concentrations meeting EPA cleanup guidelines (*9, 10*).

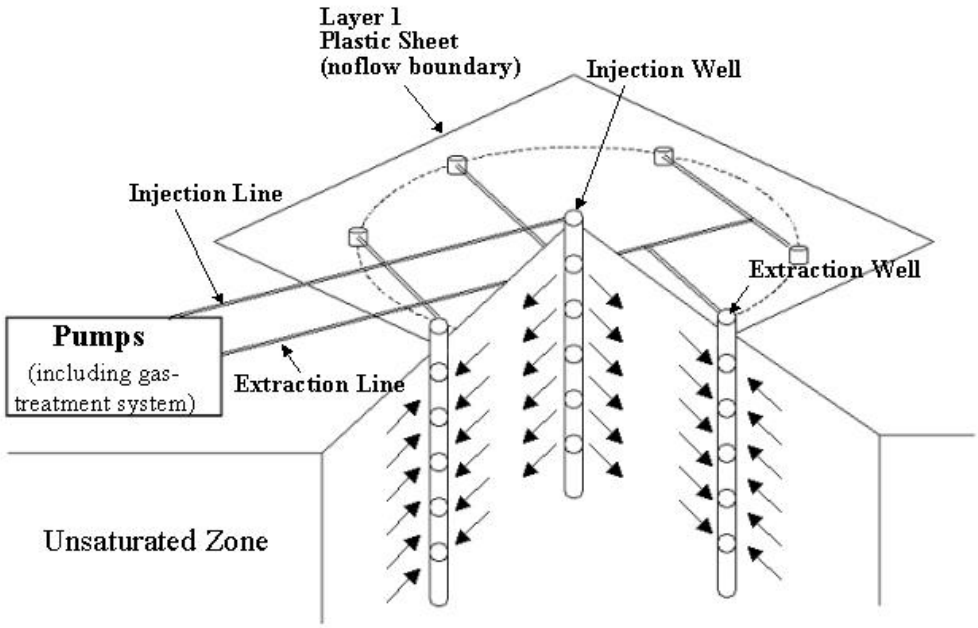

Figure 2-1. ISGR vadose zone treatment concept. (*9*)

2.2. Chromium Chemistry

2.2.1. Chromium speciation

Oxidation states of chromium in the environment range from -II to +VI (*3*), but only the +III and +VI states are stable under conditions in most natural waters. Cr(VI) is known to be more toxic to human, animals, and plants (*4*). Cr(VI) is also frequently encountered in the environment, but it is unstable in the presence of electron donors such as Fe(II) and organic matter with oxidizable groups. Major forms of Cr(VI) in natural waters are $HCrO_4^-$ and CrO_4^{2-} (*6, 11*). Distribution of these species according to pH is described by the following equations (*12*).

$$H_2CrO_4^0 = HCrO_4^- + H^+ \qquad K_{a,1} = 10^{0.86} \tag{2-1}$$

$$HCrO_4^- = CrO_4^{2-} + H^+ \qquad K_{a,2} = 10^{-6.51} \tag{2-2}$$

Thus, CrO_4^{2-} is predominant above pH 6.5, $H_2CrO_4^0$ predominates only if the pH is below 0.9, and $HCrO_4^-$ predominates in the pH range 0.9 and 6.5. When pH is low and the total concentration of Cr(VI) is greater than 10 mM, $HCrO_4^-$ dimerizes to form dichromate (*12*).

$$2\ HCrO_4^- = Cr_2O_7^{2-} + H_2O \qquad K = 10^{-1.54} \tag{2-3}$$

The dominance of the chromate ions ($HCrO_4^-$ and CrO_4^{2-}) in chromium-contaminated waters is recognized by the yellow color imparted to the water in concentrations above 1 mg/L. The presence of dichromate is seen as an orange color in contaminated water.

The predominance form of Cr(III) at pH less than 3 is Cr^{3+}. As pH increases, the hydrolysis of Cr(III) occurs and the most important species are $CrOH^{2+}$, $Cr(OH)_3^0$, and $Cr(OH)_4^-$, with $Cr(OH)_2^{2-}$ occurring in the very narrow pH band between 6.27 and 6.84 (*8*).

Natural Cr(VI) minerals are very scarce in nature because of their high solubility and their requirement for oxidizing conditions. Meanwhile, Cr(III) minerals are significant controls for dissolved chromium under moderately oxidizing to reducing conditions. $Cr(OH)_3(s)$ is probably the main Cr solubility-controlling phase in natural environments. If Fe(III) is present, amorphous [Fe(III), Cr(III)] hydroxide will also form (*6, 8*). This mixed hydroxide readily forms at room temperature and behaves as a solid solution $(Cr_xFe_{1-x})(OH)_3$ (ss). For typical natural conditions, the mole fraction (x) of chromium will be low (around 1 %).

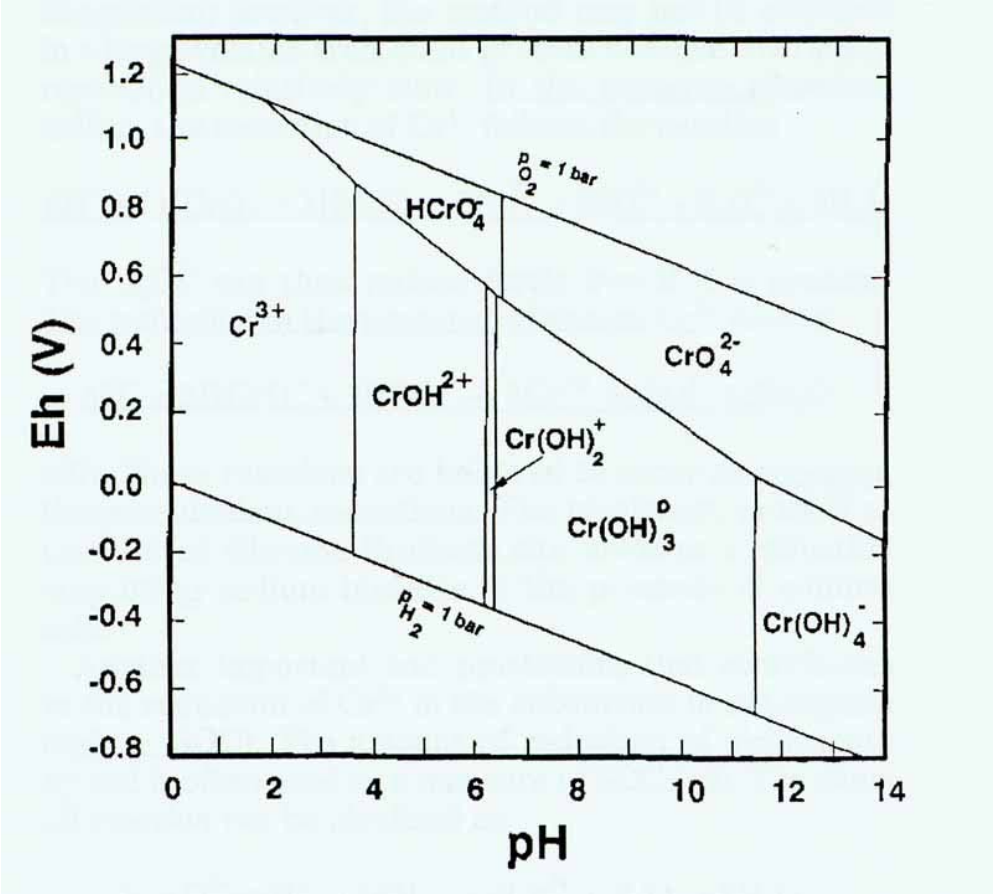

Figure 2-2. Eh-pH diagram for aqueous chromium species in a chromium-H_2O system (*8*).

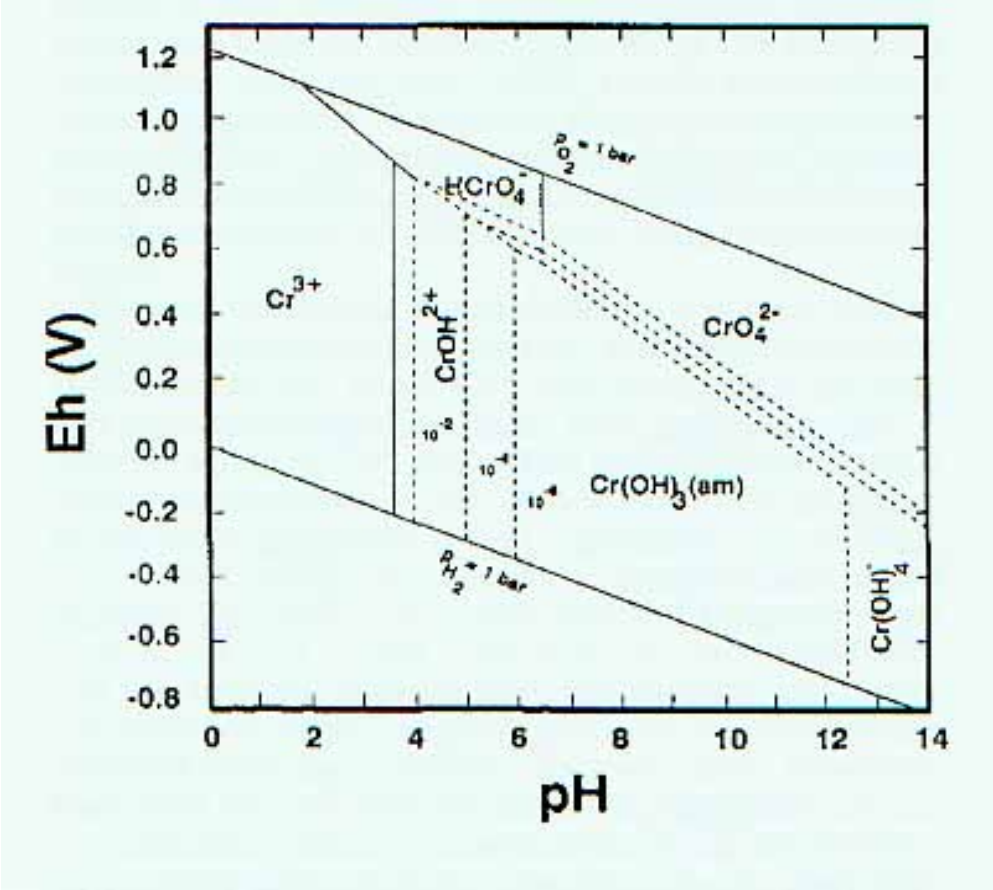

Figure 2-3. Eh-pH diagram for aqueous chromium species in equilibrium with amorphous $Cr(OH)_3$(s) in chromium-H_2O system. The dashed zone represents the domain of stability of $Cr(OH)_3$(s) for 10^{-2}, 10^{-4}, and 10^{-6} M of total dissolved Cr (*8*).

2.2.2. Oxidation-reduction of chromium

Cr(VI) is known to be reduced by Fe(II) (*13-21*), soil organic matter (*22*), including humic acid (*23, 24*) and fulvic acid (*25, 26*), cow manure (*22*), Mn(II) (*18*), and sulfides (*13, 27*).

Chromium reduction by Fe(II) is of interest in that Fe(II) is found in various types of soils and reduction by Fe(II) has been observed in many experiments in soil-water systems. The reduction of Cr(VI) by Fe(II) can be described by the overall reaction:

$$Cr(VI) + 3Fe(II) \rightarrow Cr(III) + 3Fe(III) \qquad (2\text{-}4)$$

Fe(II) could be released from primary silicates and oxides, such as muscovite and biotite, and secondary layer silicates, such as vermiculite, illite, smectites, and chlorite. Better dissolution of Fe(II) was observed with the increase in the concentration of anions such as sulfate which form complexes with Fe(II). Usually, Fe(II) is more easily supplied from minerals during the early stage of their weathering process. The reduction of Cr(VI) results in the formation of $Cr(OH)_3(s)$ and $(Cr,Fe)(OH)_3(ss)$. The low solubility of these precipitates results in aqueous concentrations of Cr(III) concentration below the drinking water limit of 10^{-6} M in the pH range between pH 5.0 and pH 11.0 (*8, 15, 16*).

Many experimental studies have confirmed that the reduction of Cr(VI) is favored under acidic conditions (*13, 14, 16, 28, 29*). Acidic environments enhance the dissolution of Fe(II) from soil minerals and the reduction of Cr(VI) by organic matter (*15, 16*). Acidic conditions also enhance the complexation of Fe(II) by anions, leading to more dissolution of Fe(II) and sequentially more reduction (*15*). Eary and Rai (*14*)

achieved significant reduction of Cr(VI) using Fe(II) at the pH range of 2 to 10, whereas Bloomfield and Pruden (*29*) reported that considerable reduction by soil organic matter occurred only at pH values between 5 and 9 in their experiments.

Another important soil constituent that contributes to the reduction of Cr(VI) in the subsurface is soil organic carbon (SOC). The amount of reduction of dichromate by soil is often used as a measure of SOC (*8*). The overall reaction can be idealized as

$$2Cr_2O_7^{2-} + 3C^0 + 16H^+ \rightarrow 4Cr^{3+} + 3CO_2 + 8H_2O \qquad (2\text{-}5)$$

The presence of SOC has been demonstrated to reduce Cr(VI) at pH above 7.0 (22, *29*). However, the reaction consumes hydrogen ions and therefore is likely to be more rapid in acidic environments than in neutral or alkaline environments. In many soils, a substantial fraction of the SOC is in the form of humic substances: humic acid (HA), fulvic acid (FA), and humin. Redox reactions involving HA and FA have been studied for a number of redox couples including Mo(VI)/Mo(IV), V(V)/V(IV), Fe(III)/Fe(II), Hg(II)/Hg(0), and I(0)/I(-I) (*30-35*). These studies show that FA is a better reducing agent than HA, but that both have the potential for reducing Cr(VI).

Cr(VI) can also be reduced by reduced sulfur compounds, including those that occur as gases at room temperature (SO_2, H_2S) (*6-10, 27, 36-38, 39-40*). Reduction by SO_2 at low pH is a common treatment method for Cr(VI) in industrial wastewater (*36-38*). At pH values below pH 4, the reaction is very rapid with half-time less than 1 minute (*36*). As pH increases, the rate decreases, resulting in a half-time of about 45 minutes at pH 7 (*37*). The effect of pH has been attributed to how pH affects the distribution of species formed when SO_2 dissolves in water (S(IV) species). When SO_2 dissolves in water, it

produces sulfurous acid (H_2SO_3), which dissociates to form HSO_3^- and SO_3^{2-}. The equilibrium coefficients for these reactions are $10^{-1.81}$ and $10^{-6.91}$ (*41*). This means that the uncharged form will dominate at pH < 1.81, the singly charged species will dominate at 1.81 < pH < 6.91, and the doubly charged species will dominate at pH > 6.91. Higher concentrations of S(IV) species in solution increase the rate of Cr(VI) reduction, but data is not available to quantify the relationship (*37*). The overall reaction is believed to be the result of a linear combination of the following two reactions (*39*).

$$2\ HCrO_4^- + 4\ HSO_3^- + 6\ H^+ = 2\ Cr^{3+} + 2\ SO_4^{2-} + S_2O_6^{2-} + 6\ H_2O \qquad (2\text{-}6)$$

$$2\ HCrO_4^- + 3\ HSO_3^- + 5\ H^+ = 2\ Cr^{3+} + 3\ SO_4^{2-} + 5\ H_2O \qquad (2\text{-}7)$$

In the presence of excess S(IV), the reduction of Cr(VI) is favored by the reaction (2-6), and the reduction in the presence of excess Cr(VI) is favored by the reaction (2-7) (*8*). These equations predict that the ratio of S(IV) oxidized to Cr(VI) reduced will vary between 1.5 and 2.0 as has been reported (*39*).

2.2.3. Other processes related with chromium

Soluble ionic forms of Cr(IV) formed in or added to soils or natural waters are also removed by leaching, adsorption, and uptake by living cells (*42*).

Chromate ions can be adsorbed by Mn, Al and Fe oxides, clay minerals and natural soils and colloids and it is favored by acidity or other factors that increase the positive charges on soil colloids (*42*). Adsorption of Cr(VI) is a surface complexation reaction between aqueous chromates and hydroxyl-specific surface sites (*43, 44*). At dilute concentrations, adsorption of Cr(VI) increases as pH decrease and this result suggests

that Cr(VI) adsorption is favored on adsorbents that are positively charged at low to neutral pH (*6*). A larger ionic strength decreases the adsorption of chromate and this is due to a lowering in CrO_4^{2-} activity, a reduction in coulombic attraction for chromate species on solid surfaces and/or to the presence of competing anions (*6*). Competing anions have a drastic effect on Cr(VI) adsorption. In natural environments, chromate sorption will be highly influenced by the electrostatic conditions imposed by the common major anions, which bind to the solid surfaces. Adsorption of Cr(VI) can therefore be expected to be minimal in groundwater and soil (*6*).

Leaching processes have not been fully acknowledged, but reporting of Cr(VI) in groundwater shows that leaching occurs to remove Cr(VI). And, a trace amount of chromium is found in plants and it possibly enters by root uptake of Cr(VI) (*45, 46*).

CHAPTER III

METHODOLOGY

3.1. Materials

Potassium dichromate (99+%, ACS grade, Aldrich) and sulfur dioxide gas (99.9+%, Aldrich) were used as reactants. Deoxygenated deionized water (water, hereafter) was prepared by taking water that was purified by a Barnstead Nanopure system and purging it for at least 12 hours with the atmosphere of the anaerobic chamber (Coy Laboratory Products), which contained 95% N_2 and 5% H_2. Cr(VI) stock solution (1000 mg/L) was prepared with $K_2Cr_2O_7$. Depending on the desired S(IV)/Cr(VI) ratio, 3 different S(IV) stock solutions (30, 75, or 300 mg/L) were prepared immediately before the initiation of each experiment by dissolving sulfur dioxide gas into water. Potassium dihydrogen phosphate (99+%, Aldrich) and sodium bicarbonate (99.7+%, Aldrich) were used for the preparation of a 0.025 M buffer solution that was used to maintain pH 6 or 7. The buffer solution was prepared in the anaerobic chamber.

Surface soil, collected by Dr. Inseong Hwang from a ranch at Texas A&M University, College Station, Texas, was used for the experiment of Cr(VI) reduction in soil (*47*). The soil is an alluvium of the Brazos River and is classified as Silawa loamy sand. It was air-dried and screened to particle sizes below 0.425 mm (No. 40 mesh). There was no effort taken during collection, storage, drying, and sieving the soil to maintain the redox state it had in-situ.

3.2. Analytical procedures

3.2.1. Stoichiometry and kinetics of Cr(VI) reduction in water

Diphenylcarbazide method (*48*) was used for aqueous Cr(VI) analysis (UV-VIS spectrophotometer, Hewlett Packard Agilent 8453). Before the Cr(VI) measurement, the remaining S(IV) was oxidized by adding 0.5 mM cobalt(II) and bubbling air through the solution to provide oxygen. This procedure removed the possibility of a reaction between S(IV) and Cr(VI) in the low-pH solutions used during analysis. If such a reaction was to occur, it would result in errors in Cr(VI) measurement. The effectiveness of this procedure in removing S(IV) was tested using all conditions of later kinetic experiments (2 pH values x 3 initial S(IV)/Cr(VI) ratios). After the treatment with cobalt(II) and oxygen, the concentration of S(IV) was found to be below the detection limit (0.03 mg/L) for all conditions. The possible effect of cobalt(II), oxygen, and reaction products, (Cr(III), S(V/VI)), on Cr(VI) measurement was also examined and it was found that there they had no influence on the measurment. This result shows that this colorimetric method for Cr(VI) analysis, including the step of S(IV) oxidation by cobalt(II) and oxygen, provides accurate measurement of Cr(VI) (table 3-1). The method detection limit (MDL) was calculated as the product of the standard deviation of replicate measurements and student's t-value at a 99% confidence level. Precision was expressed as percentile relative standard deviation (% RSD). Accuracy was expressed as average percent recovery (% recovery).

The phenanthroline method (*48*) was used for aqueous S(IV) analysis (UV-VIS spectrophotometer, Hewlett Packard Agilent 8453). Prior to S(IV) analysis, Cr(VI) was removed by precipitation with 0.015 mM thallium(I) and filtration by 0.45-μm membrane filtration. The effectiveness of Cr(VI) removal by the procedure was tested using conditions of all later kinetic experiments (2 pH values x 3 initial S(IV)/Cr(VI) ratios). More than 99.5% of initial Cr(VI) was removed by treatment with thallium(I). The possible effect of thallium(I) on S(IV) measurement was also examined and it was found to have an insignificant influence on the measurment (1~2% decrease of initial concentration). This result shows that this colorimetric method for S(IV) analysis, including the step of Cr(VI) removal by thallium(I), provides accurate measurement (table 3-2).

A kinetic model was investigated to describe stoichiometry and kinetics of Cr(VI) reduction by SO_2. Kinetic coefficient for the models was calculated using non-linear regression. The standard error of the estimate was used as a measure of goodness of fit.

Table 3-1. Quality assurance/quality control for Cr(VI) analysis in water.

	Quality objectives	Experiments
MDL, mg/L Cr(VI)	0.1	0.01 - 0.03
Precision, % RSD	< 15	0.3 – 1
Accuracy, % recovery	70 - 120	99 – 100

Table 3-2. Quality assurance/quality control for S(IV) analysis in water.

	Quality objectives	Experiments
MDL, mg/L S(IV)	0.03	0.01
Precision, % RSD	< 15	1
Accuracy, % recovery	70 - 120	97 – 98

3.2.2. Stoichiometry and kinetics of Cr(VI) reduction in soil

The phenanthroline method was used for gaseous S(IV) analysis. For measurement of gaseous SO_2, the procedure is same as that of aqueous S(IV), except that a portion of gas sample is transferred to the absorbing solution rather than an aqueous sample. This colorimetric method of analysis provides accurate measurement of gaseous S(IV) (table 3-3).

Cr(VI) was desorbed from soil with sulfate solution and was analyzed in the solution by the diphenylcarbazide method described previously. After S(IV) measurement, the sample was flushed with air for 1 min to remove the remaining SO_2 gas. After flushing with air, the amount of S(IV) detected was insignificant (less than 3 % of initial S(IV) concentration). Cr(VI) extraction using sulfate solution followed air flushing. For Cr(VI) extraction, 1 M sulfate solution was added into the sample at rate of 5 mg/g soil and shaken using a tumbler for 30 min. Cr(VI) in soil was successfully extracted (more than 98 % of initial Cr(VI) concentration). The result shows that this colorimetric method of analysis provides accurate measurement of Cr(VI) in soils (table 3-4).

A kinetic model was investigated to describe stoichiometry and kinetics of Cr(VI) reduction by SO_2. Kinetic coefficient for the models was calculated using non-linear regression. The standard error of the estimate was used as a measure of goodness of fit.

Table 3-3. Quality assurance/quality control for S(IV) analysis in gas.

	Quality objectives	Experiments
MDL, vol % SO_2	0.03	0.03
Precision, % RSD	< 15	2
Accuracy, % recovery	70 - 120	98

Table 3-4. Quality assurance/quality control for Cr(VI) analysis in soil.

	Quality objectives	Experiments
MDL, mg/kg Cr(VI)	0.1	0.07
Precision, % RSD	< 15	0.3
Accuracy, % recovery	70 - 120	95

3.3. Experimental procedures

A batch reactor system consisting of 40 ml borosilicate glass vials (Kimble) with an open-top screw cap and PTFE film lined rubber septum was used. Experiments were conducted in these reactors to characterize the kinetics and stoichiometry of Cr(VI) reduction in water and soil.

3.3.1. Stoichiometry and kinetics of Cr(VI) reduction in water

The effects of pH (pH 6, 7) and S(IV)/Cr(VI) ratio (0.5, 1.25, 5) on stoichiometry and kinetics of Cr(VI) reduction were examined. Batch reactors were used with solutions buffered with 0.025 M phosphate-carbonate mixed buffer. Buffered solutions were adjusted to designed pH values with 1+1 HCl or 1 N NaOH solution. Cr(VI) concentration in the sample solution was 10 mg/L, and S(IV) concentration was 3, 7.5, or 30 mg/L, depending on the desired initial S(IV)/Cr(VI) ratio.

The experimental and analytical procedures used in these experiments are outlined in figure 3-1. All steps of the experimental procedure, except preparation of S(IV) stock solution, were conducted in an anaerobic chamber. The glass vials and closures were equilibrated in an anaerobic chamber before preparing samples.

Samples were taken at times separated by a geometric progression with the last time predicted to result in 90 % conversion. All possible combinations of experimental variables were investigated (6 experiments).

3.3.2. Stoichiometry and kinetics of Cr(VI) reduction in soil

The effect of water content (0.01, 0.05, 0.25 g/g) on stoichiometry and kinetics of Cr(VI) reduction was investigated in batch reactors. Each reactor contained 2 g Silawa soil that was spiked with Cr(VI) stock solution to achieve a concentration of 1 mg/g. A mixture of 2 ml SO_2 gas (5 % (v/v)) and 38 ml N_2-H_2 mixed gas was added to the reactors.

The experimental and analytical procedures used in these experiments are outlined in figure 3-2. The water content and Cr(VI) concentration was controlled by adding a Cr(VI) solution with a volume that provided the desired amount of water and a concentration of Cr(VI) that provided the desired concentration of Cr(VI) in the soil (1 mg/g) (table 3-5). However, at the lowest water content (0.01 g/g), the concentration of Cr(VI) in the water needed to do this could not be achieved due to solubility limitations. In this case, additional water was added and then evaporated to achieve the desired water content. The glass vials and closures were equilibrated in an anaerobic chamber before preparing samples.

Samples were taken at times separated by a geometric progression over a time period predicted to result in 90 % conversion.

Table 3-5. Control of the water content and Cr(VI) concentration in the soil sample.

Water content	Controlling method
0.25 g/g	Add 12.5 ml Cr(VI) solution (4,000 mg/l) & mix
0.05 g/g	Add 2.5 ml Cr(VI) solution (20,000 mg/l) & mix
0.01 g/g	Add 2.5 ml Cr(VI) solution (20,000 mg/l), dry to 0.5 ml, & mix

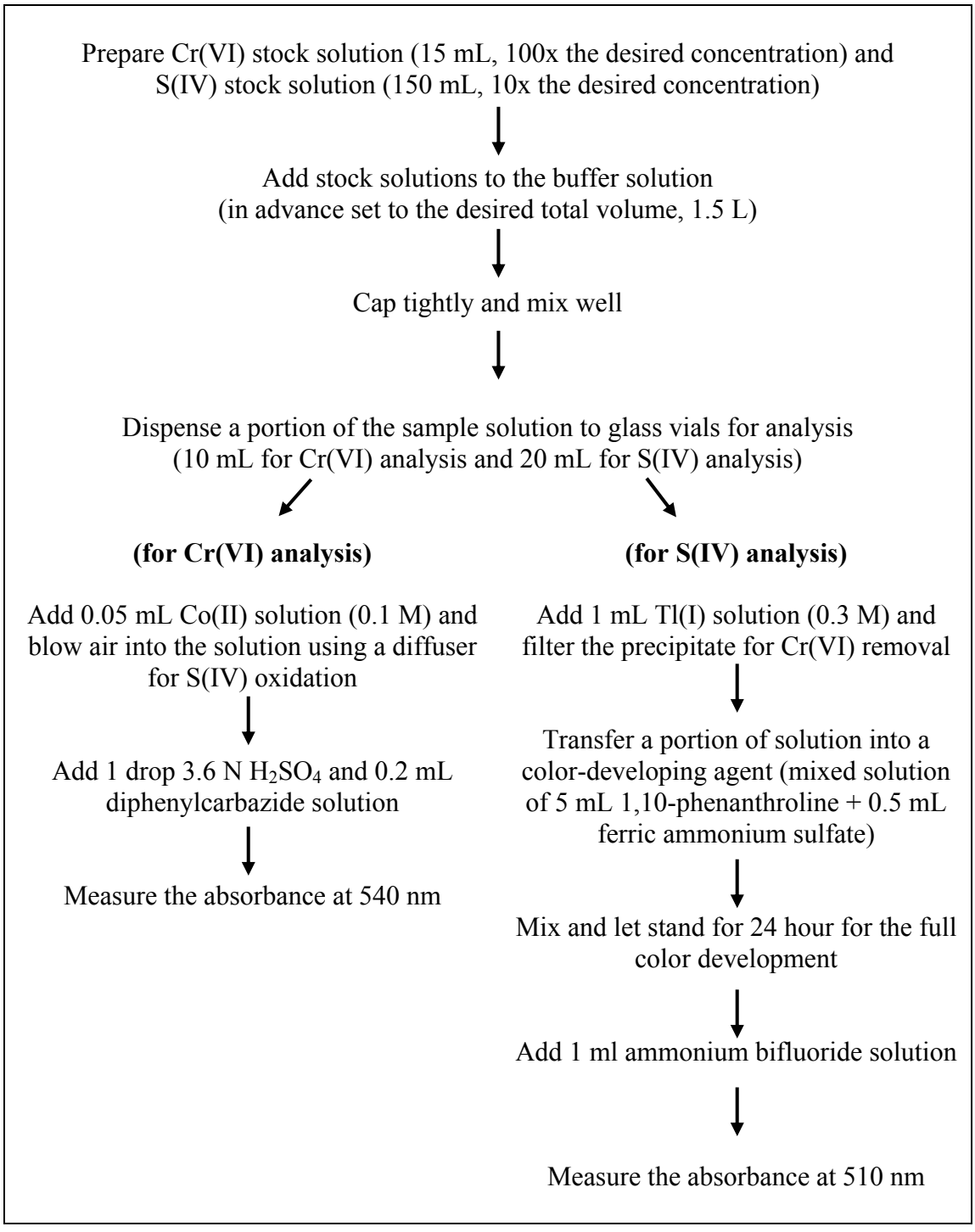

Figure 3-1. Overview of experimental and analytical procedures of the experiment for Cr(VI) reduction in water

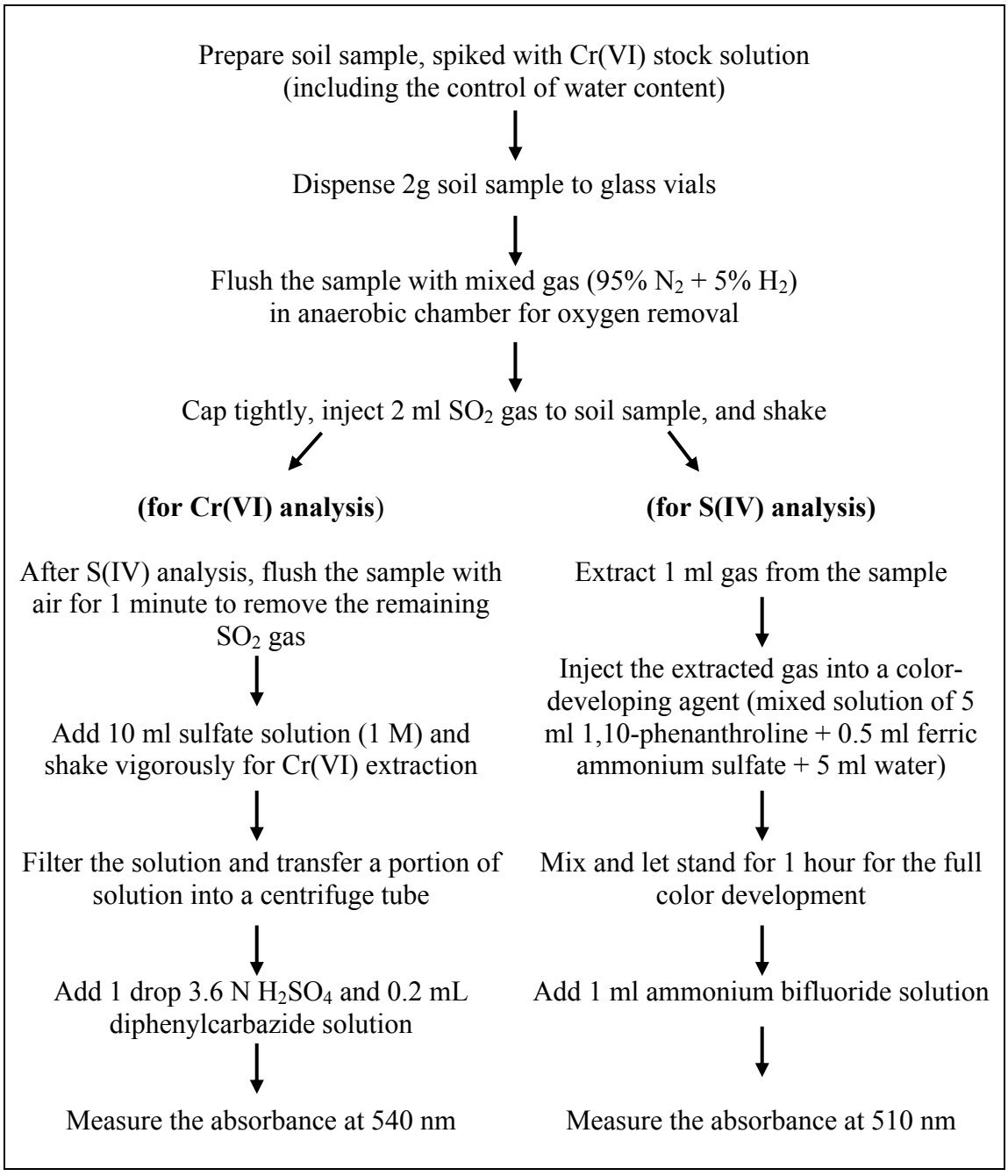

Figure 3-2. Overview of experimental and analytical procedures of the experiment for Cr(VI) reduction in soil.

CHAPTER IV

RESULTS AND DISCUSSION

4.1. Characterization of stoichiometry and kinetics of Cr(VI) reduction in water

Experiments were conducted to examine Cr(VI) reduction in water. Data on stiochiometry and kinetics of Cr(VI) reduction by SO_2 in aqueous solution at pH values near neutrality were obtained from experiments. Despite the widespread use of this process at low pH for wastewater treatment, there is very little quantitative information in the literature on the process at values of pH near pH 7 that are expected in soils. Information on the behavior of this reaction in aqueous solution will aid design and interpretation of results in soil systems. Furthermore, the effects of pH (pH 6, 7) and S(IV)/Cr(VI) ratio (0.5, 1.25, 5) were investigated.

4.1.1. Stoichiometry of Cr(VI) reduction

The stoichiometry of Cr(VI) reduction by S(IV) varies depending on the relative amounts of reactants and possibly pH. The stoichiometry of the reaction would be important in applying it in a remedial technology because it would determine the required doses of reductant. The overall stoichiometry is believed to be the result of a linear combination of the following two reactions (*39*).

$$2\ HCrO_4^- + 4\ HSO_3^- + 6\ H^+ = 2\ Cr^{3+} + 2\ SO_4^{2-} + S_2O_6^{2-} + 6\ H_2O \qquad (4\text{-}1)$$

$$2\ HCrO_4^- + 3\ HSO_3^- + 5\ H^+ = 2\ Cr^{3+} + 3\ SO_4^{2-} + 5\ H_2O \qquad (4\text{-}2)$$

The reaction (4-1) is favored at high S(IV)/Cr(VI) ratios and possibly at high pH. These equations predict that the ratio of S(IV) oxidized to Cr(VI) reduced will vary between 1.5 and 2, as has been reported (*39*).

Experiments showed stoichiometry ratios ranging between 1.6 and 1.8 (figures 4-1 through 4-6). These results (table 4-1) support the suggestion that the overall stoichiometry is the result of a linear combination of two reactions (4-1 and 4-2) in which sulfate is the stable oxidation product of sulfite and dithionate is an intermediate. Figures 4-1 through 4-6 also show that Cr(VI) and S(IV) concentrations in controls are almost constant during experiments. Thus, the loss of Cr(VI) or S(IV) by reactions such as S(IV) oxidation by oxygen is not significant in these experiments.

The results also show that pH or initial S(IV)/Cr(VI) ratio did not affect the stoichiometry of Cr(VI) reduction by sulfur dioxide.

Table 4-1. Stoichiometry of Cr(VI) reduction by sulfur dioxide. (expressed as molar ratio of S(IV) consumed versus Cr(VI) consumed)

	Initial ratio of S(IV)/Cr(VI)		
	5	1.25	0.5
pH 6	**1.8**	**1.65**	**1.6**
pH 7	**1.75**	**1.6**	**1.65**

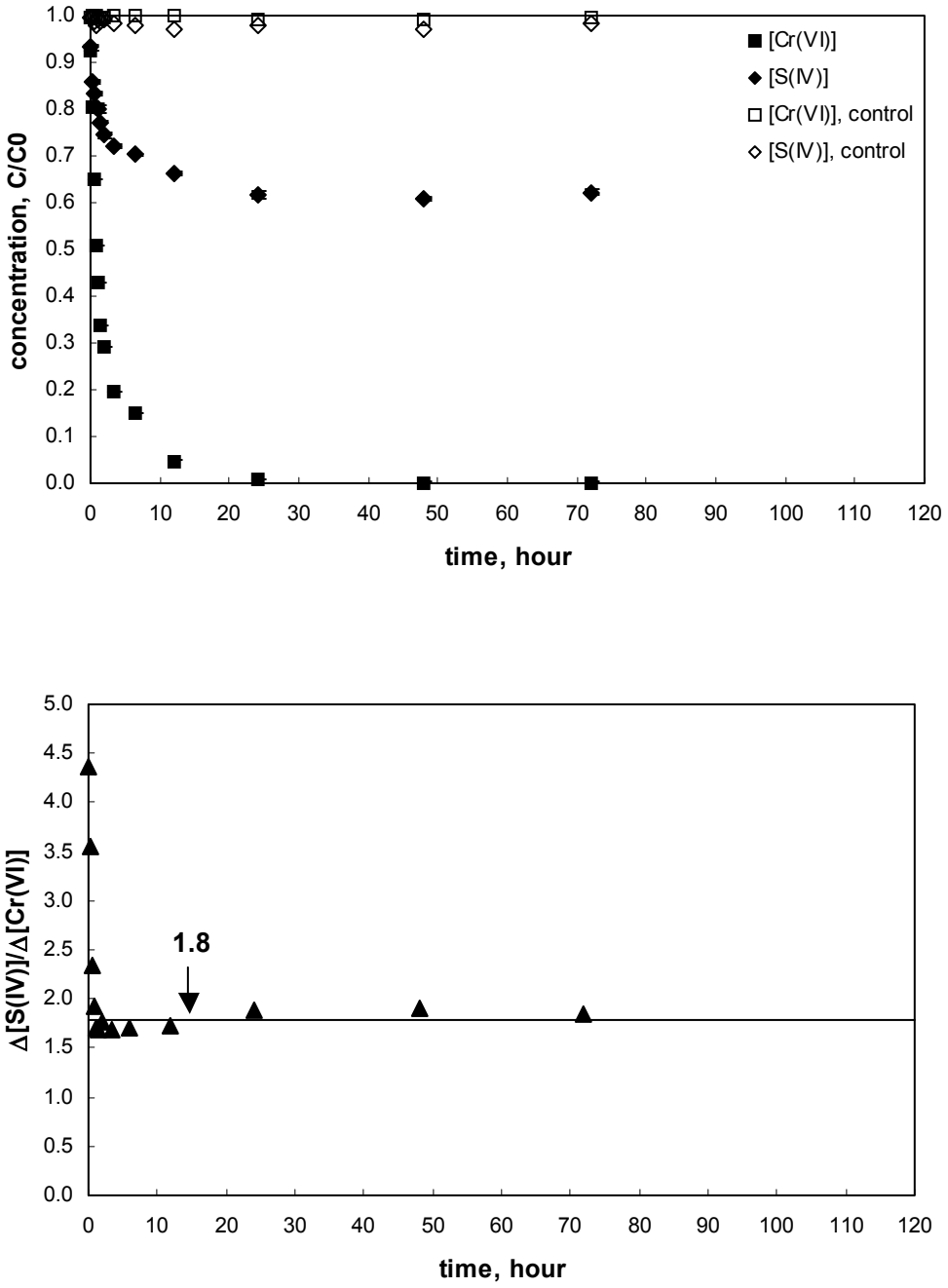

Figure 4-1. Stoichiometry of Cr(VI) reduction by sulfur dioxide (pH 6 & S(IV)/Cr(VI) ratio 5, initial concentrations [Cr(VI)] = 0.19 mM & [S(IV)] = 0.94 mM)

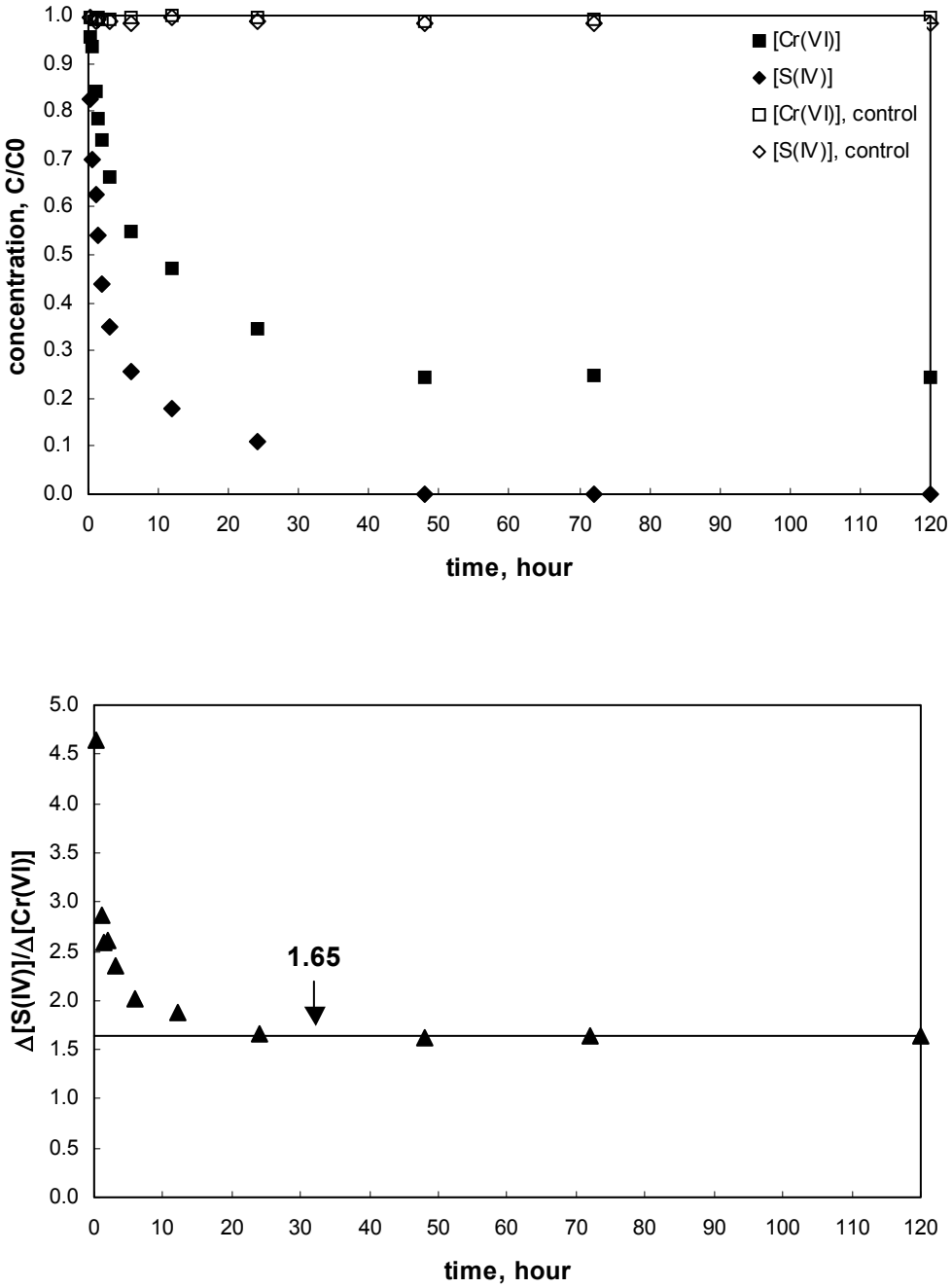

Figure 4-2. Stoichiometry of Cr(VI) reduction by sulfur dioxide (pH 6 & S(IV)/Cr(VI) ratio 1.25, initial concentrations [Cr(VI)] = 0.19 mM & [S(IV)] = 0.23 mM)

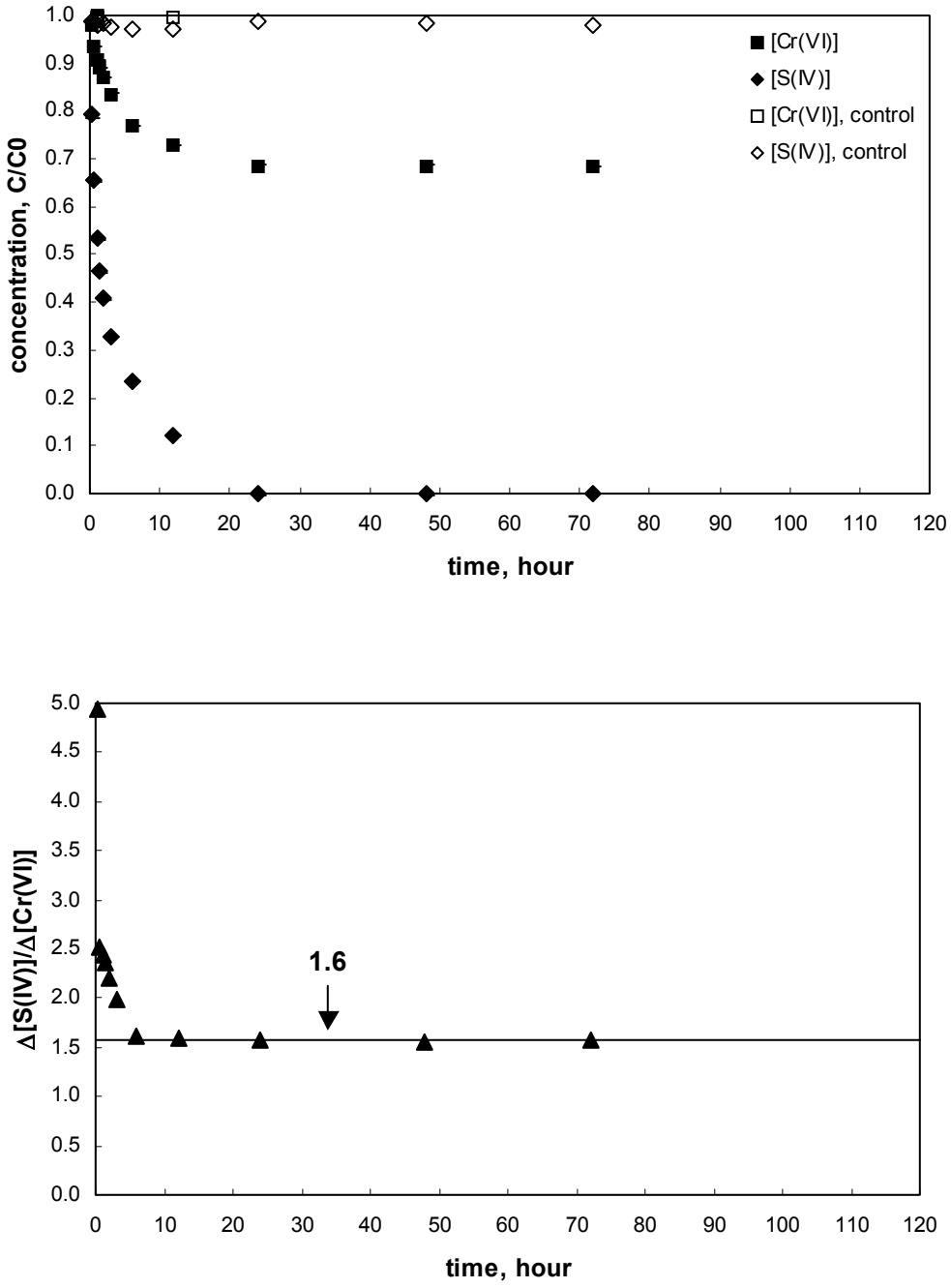

Figure 4-3. Stoichiometry of Cr(VI) reduction by sulfur dioxide (pH 6 & S(IV)/Cr(VI) ratio 0.5, initial concentrations [Cr(VI)] = 0.19 mM & [S(IV)] = 0.094 mM)

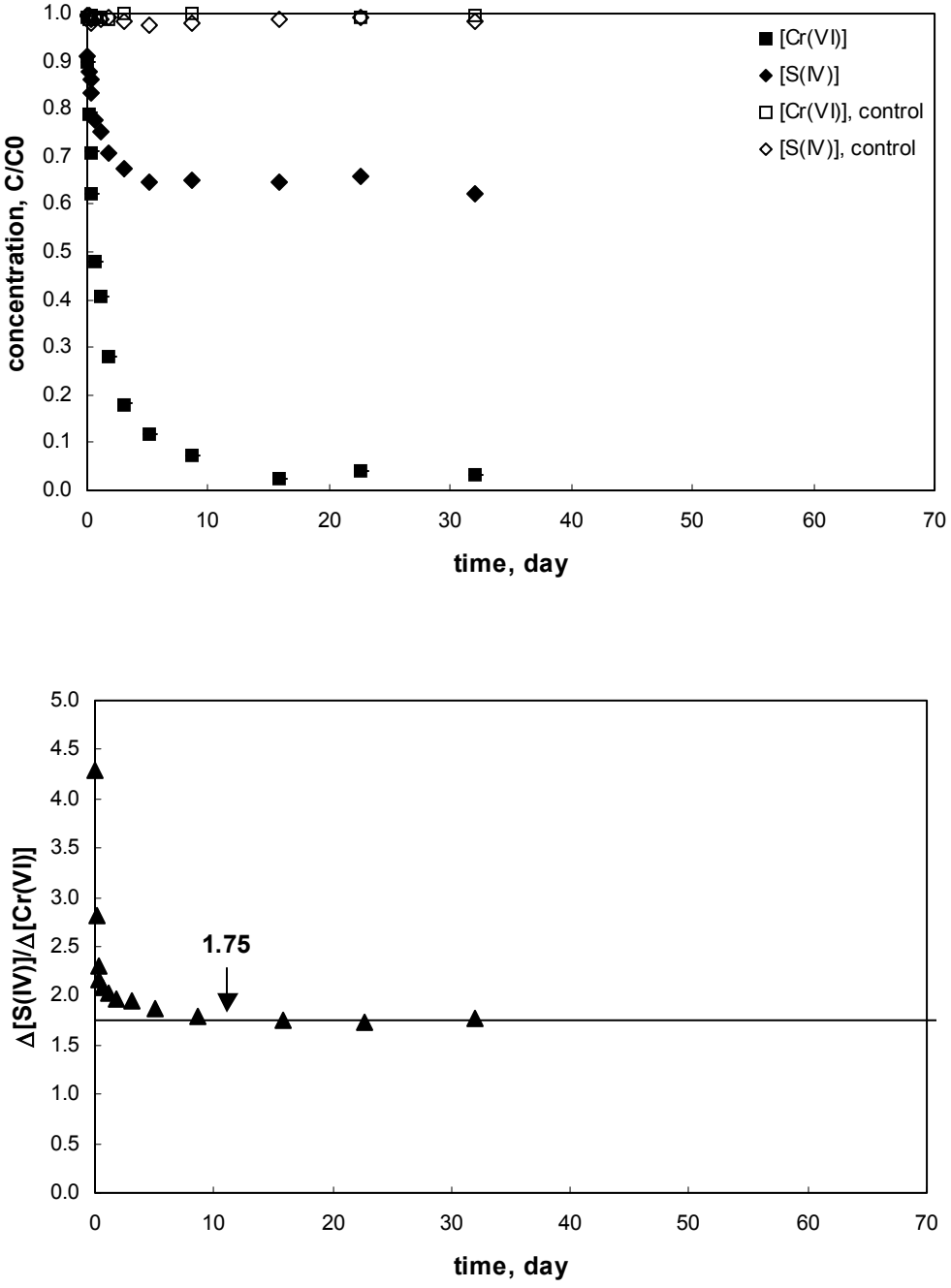

Figure 4-4. Stoichiometry of Cr(VI) reduction by sulfur dioxide (pH 7 & S(IV)/Cr(VI) ratio 5, initial concentrations [Cr(VI)] = 0.19 mM & [S(IV)] = 0.94 mM)

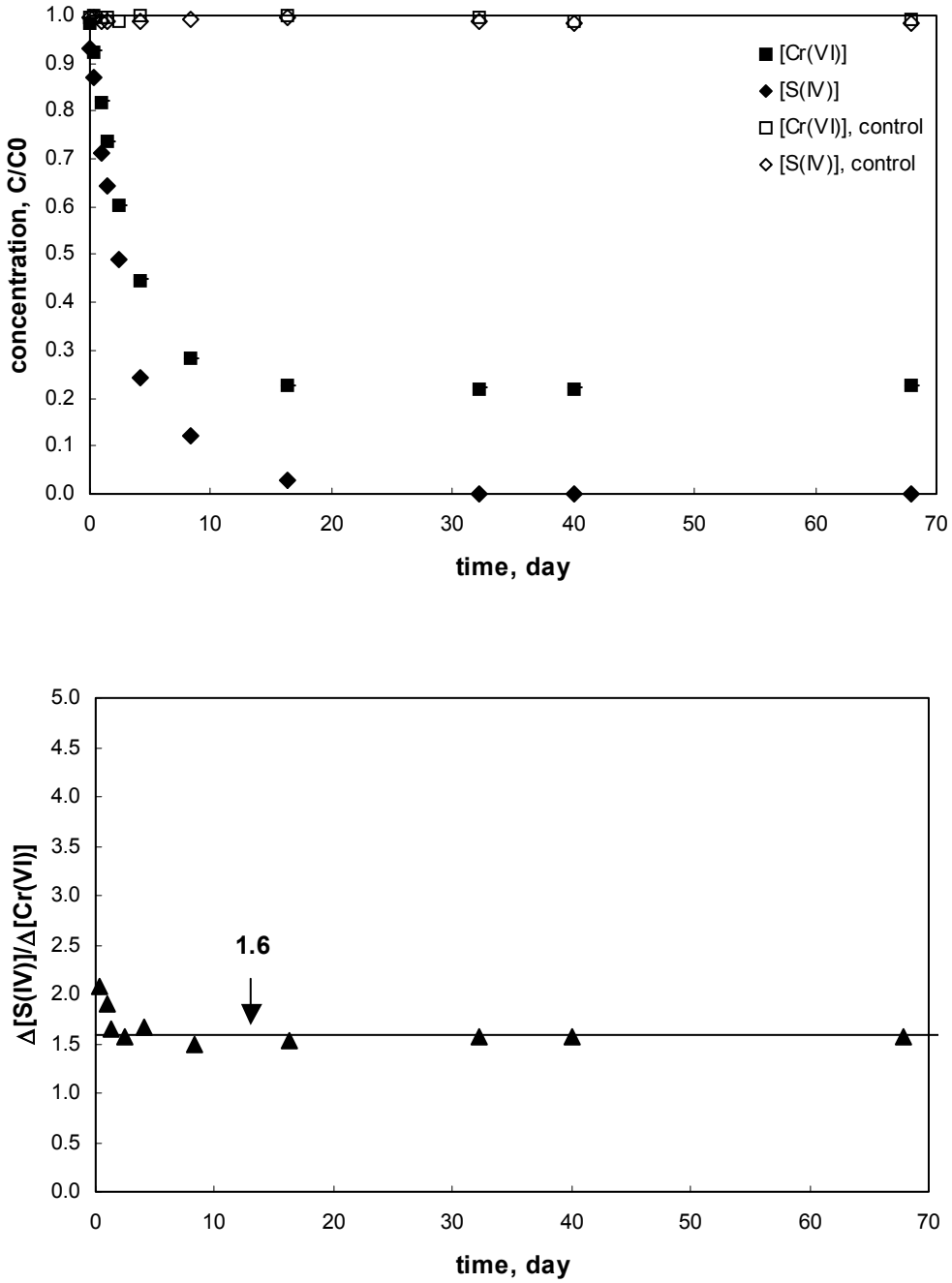

Figure 4-5. Stoichiometry of Cr(VI) reduction by sulfur dioxide (pH 7 & S(IV)/Cr(VI) ratio 1.25, initial concentrations [Cr(VI)] = 0.19 mM & [S(IV)] = 0.23 mM)

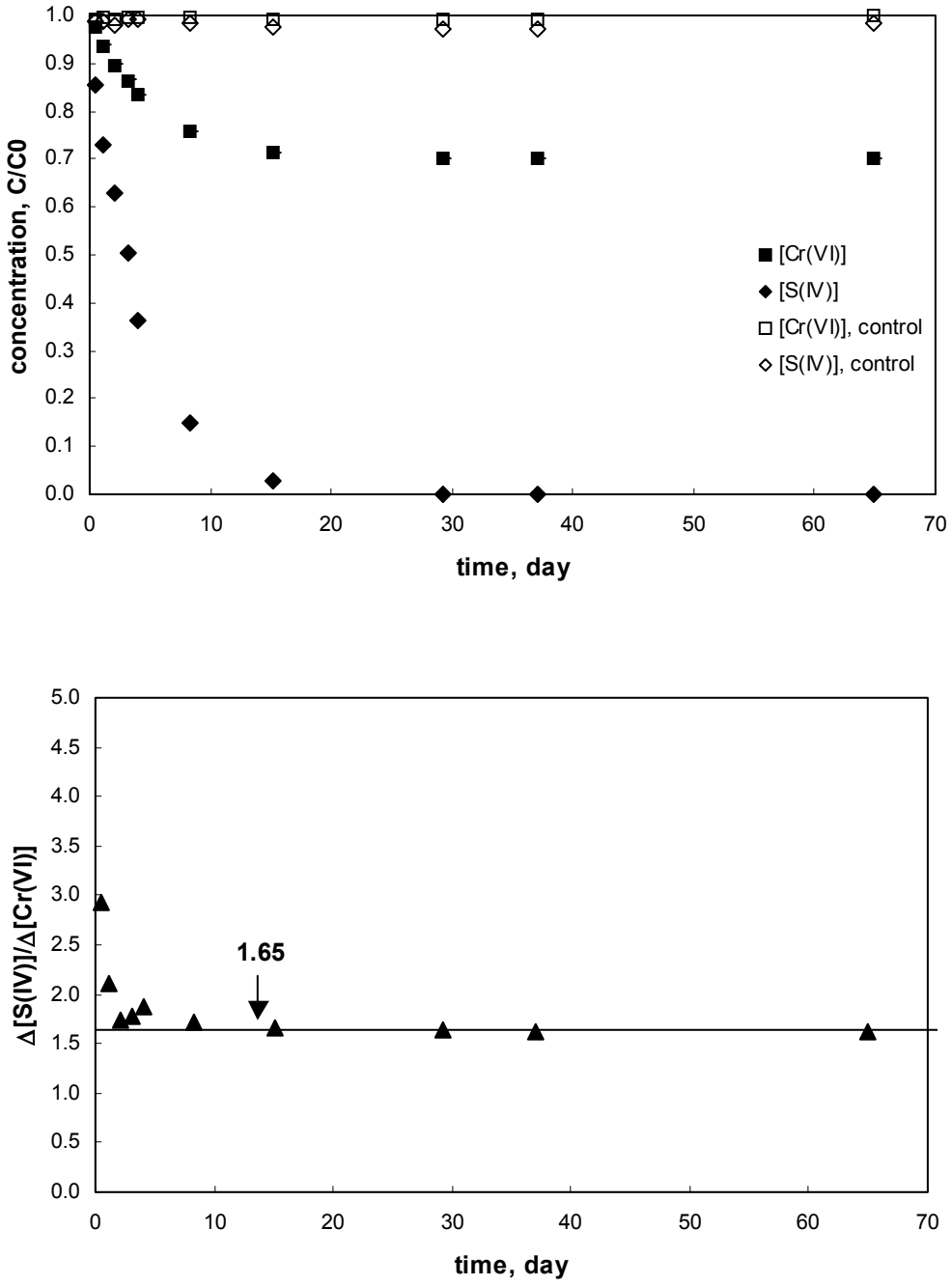

Figure 4-6. Stoichiometry of Cr(VI) reduction by sulfur dioxide (pH 7 & S(IV)/Cr(VI) ratio 0.5, initial concentrations [Cr(VI)] = 0.19 mM & [S(IV)] = 0.094 mM)

4.1.2. Kinetics of Cr(VI) reduction

A kinetic model for Cr(VI) reduction could be hypothesized based on the observed stoichiometry. This model considers two reactions.

$$Cr(VI) + 3S(IV) \xrightarrow{k1} Cr(III) + 3S(V) \quad (4\text{-}3)$$

$$Cr(VI) + 3S(V) \xrightarrow{k2} Cr(III) + 3S(VI) \quad (4\text{-}4)$$

Rate equations for each reaction can be expressed using general power law relationships and combined with material balances for a batch reactor to generate equations 4-3 and 4-4.

$$\frac{d[Cr(VI)]}{dt} = -k_1[Cr(VI)]^{x1}[S(IV)]^{y} - k_2[Cr(VI)]^{x2}[S(V)]^{z} \quad (4\text{-}5)$$

$$\frac{d[S(IV)]}{dt} = -3k_1[Cr(VI)]^{x1}[S(IV)]^{y} \quad (4\text{-}6)$$

$$\frac{d[S(V)]}{dt} = 3k_1[Cr(VI)]^{x1}[S(IV)]^{y} - 3k_2[Cr(VI)]^{x2}[S(V)]^{z} \quad (4\text{-}7)$$

The kinetic parameters, k_1 and k_2, were obtained by conducting nonlinear regression of concentrations of Cr(VI), S(IV), and S(V) using MATLAB® (MathWorks Inc.) (APPENDIX B). A range of reaction orders were assumed for these regressions and the best results were obtained when the reaction was assumed to be second-order with respect to [Cr(VI)] and first-order with respect to [S(IV)], and [S(V)].

At pH values below pH 4, Cr(VI) reduction by SO_2 is very rapid with half-time less than 1 minute (*36*). As pH increases, the rate decreases, resulting in a half-time of about 45 minutes at pH 7 (*37*). In the presence of excess S(IV), experiments also show that the reaction is rapid, with the half-time of about 45 minutes at pH 6 and about 16 hours at

pH 7. The calculation, using MATLAB, showed fairly good fit on data (figures 4-7 and 4-8). The rate coefficients, k_1 and k_2, at pH 6 and 7 were 4.5 (± 10%), 25 (± 29%) ($mM^{-2}h^{-1}$) and 0.25 (± 9.4%), 1.1 (± 30%) ($mM^{-2}h^{-1}$), respectively. (table 4-2)

Table 4-2. Kinetics of Cr(VI) reduction by sulfur dioxide. (expressed as rate coefficient in unit of $mM^{-2}h^{-1}$)

	k_1	k_2
pH 6	**4.5 (± 10%)**	**25 (± 29%)**
pH 7	**0.25 (± 9.4%)**	**1.1 (± 30%)**

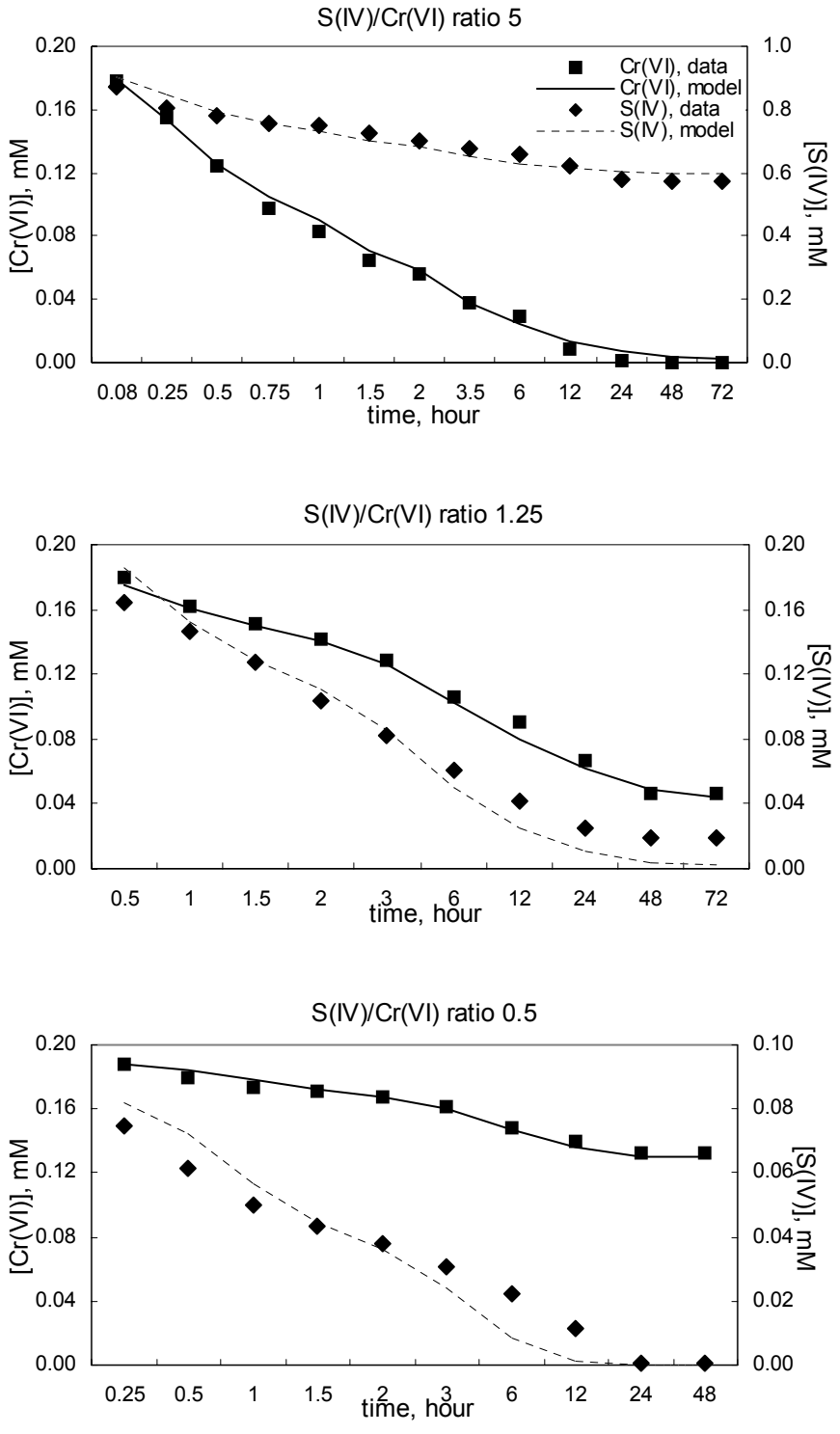

Figure 4-7. Kinetics of Cr(VI) reduction by sulfur dioxide in water (pH = 6)

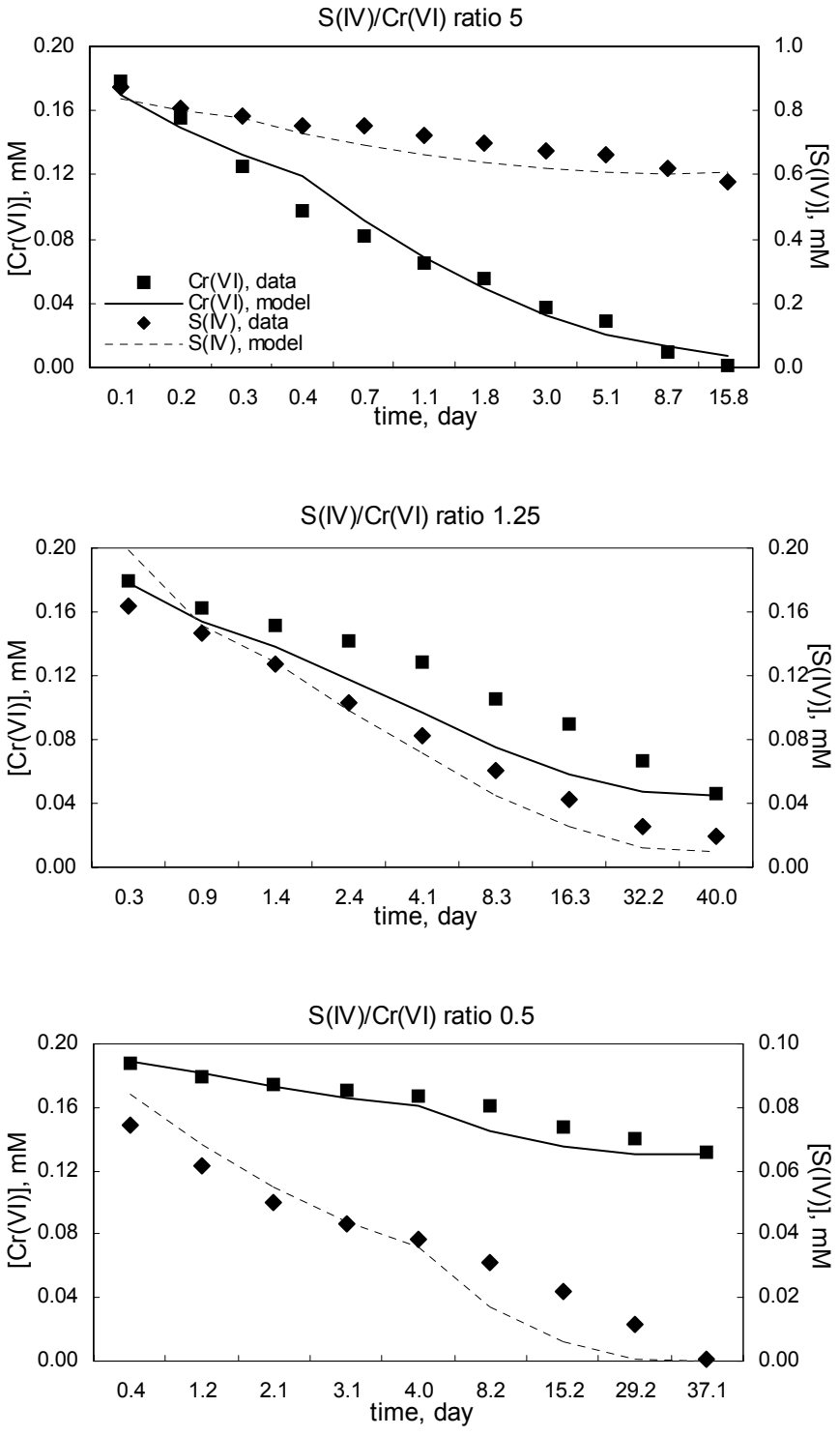

Figure 4-8. Kinetics of Cr(VI) reduction by sulfur dioxide in water (pH = 7)

4.1.3. The effect of pH

Table 4-1 showed that pH does not affect the stoichiometry of Cr(VI) reduction by SO_2. Meanwhile, pH has some effects on the kinetics of the reaction. The reaction rate decreases as pH increases. Experiments show that the rate at pH 7 is lower than at pH 6 by one order of magnitude. Generally, the rate of Cr(VI) reduction decreases with an increase in pH value (*36*). The reduction is accomplished with sulfurous acid and not with the bisulfite ion. The portion of undissociated sulfurous acid decreases as pH increases and thus, the application of excessive amounts of sulfur dioxide is required to provide sufficient sulfurous acid to completely reduce Cr(VI) in the range of neutral pH (*36*).

4.1.4. The effect of S(IV)/Cr(VI) ratio

The S(IV)/Cr(VI) stoichiometric ratio was observed by Haight et al. (*39*) to range between 1.5 and 2 and this variation can be explained by a linear combination of two reactions (4-1) and (4-2). Experiments presented here showed similar ratio values, ranging between 1.6 and 1.8.

The observed stoichiometry varies with the initial S(IV)/Cr(VI) ratio. Haight et al. (*39*) reported that the ratio of S(IV) consumed to Cr(VI) consumed ranges between 1.63 and 1.95, when S(IV) is in excess, but ranges between 1.54 and 1.63, when Cr(VI) is in excess. Experiments presented here show that the stoichiometry lies in the range of 1.75 - 1.8 with initial S(IV)/Cr(VI) ratio equal to 5, and in the range of 1.6 - 1.65 with initial S(IV)/Cr(VI) ratios equal to 1.25 and 0.5. The reaction (4-1) is favored at high

S(IV)/Cr(VI) ratio and this reaction gives a higher ratio of S(IV) removed to Cr(VI) removed.

4.2. Characterization of stoichiometry and kinetics of Cr(VI) reduction in soil

Experiments were conducted to examine the stoichiometry and kinetics of Cr(VI) reduction in soil. The effects of water content were evaluated. These results could be used to predict and optimize effectiveness of remedial technologies.

4.2.1. Stoichiometry of Cr(VI) reduction

The stoichiometry of Cr(VI) reduction by S(IV) in water showed that the overall stoichiometry ratio of S(IV) oxidized to Cr(VI) reduced is the result of a linear combination of two reactions (4-1 and 4-2), and the value of the ratio ranges between 1.6 and 1.8 (table 4-1).

Meanwhile, Cr(IV) reduction in soil showed the stoichiometry ratio is almost 2 (figures 4-9 through 4-11), which is a little higher than that of the reaction in water. This indicates that all of the initial Cr(VI) was consumed during the reaction, and that the remaining S(IV) might be used by another reaction(s). One possible reaction would be S(IV) oxidation by Fe(III). Fe(III) can be provided for the reaction from soil minerals such as iron oxide. Chemical analysis of the soil used in these experiments (*47*) shows that the amount of Fe(III) in soil is 5.8 mg/g, which is enough for the reaction between S(IV) and Fe(III). The standard redox potential of Fe(III)/Fe(II) is higher (E_0 = 0.77 V)

than that of S(VI)/S(IV) (E_0 = 0.17 V) (*41*), so the reaction is feasible under standard conditions. Like the reaction between S(IV) and Fe(III), the reaction of S(IV) oxidation by Mn(IV) could also occur. The standard redox potential of Mn(IV)/Mn(II) is also higher (E_0 = 1.22 V) than that of S(VI)/S(IV) (*41*). Analytical data on Mn(IV) concentration in the soil used for these experiments is not available at this time.

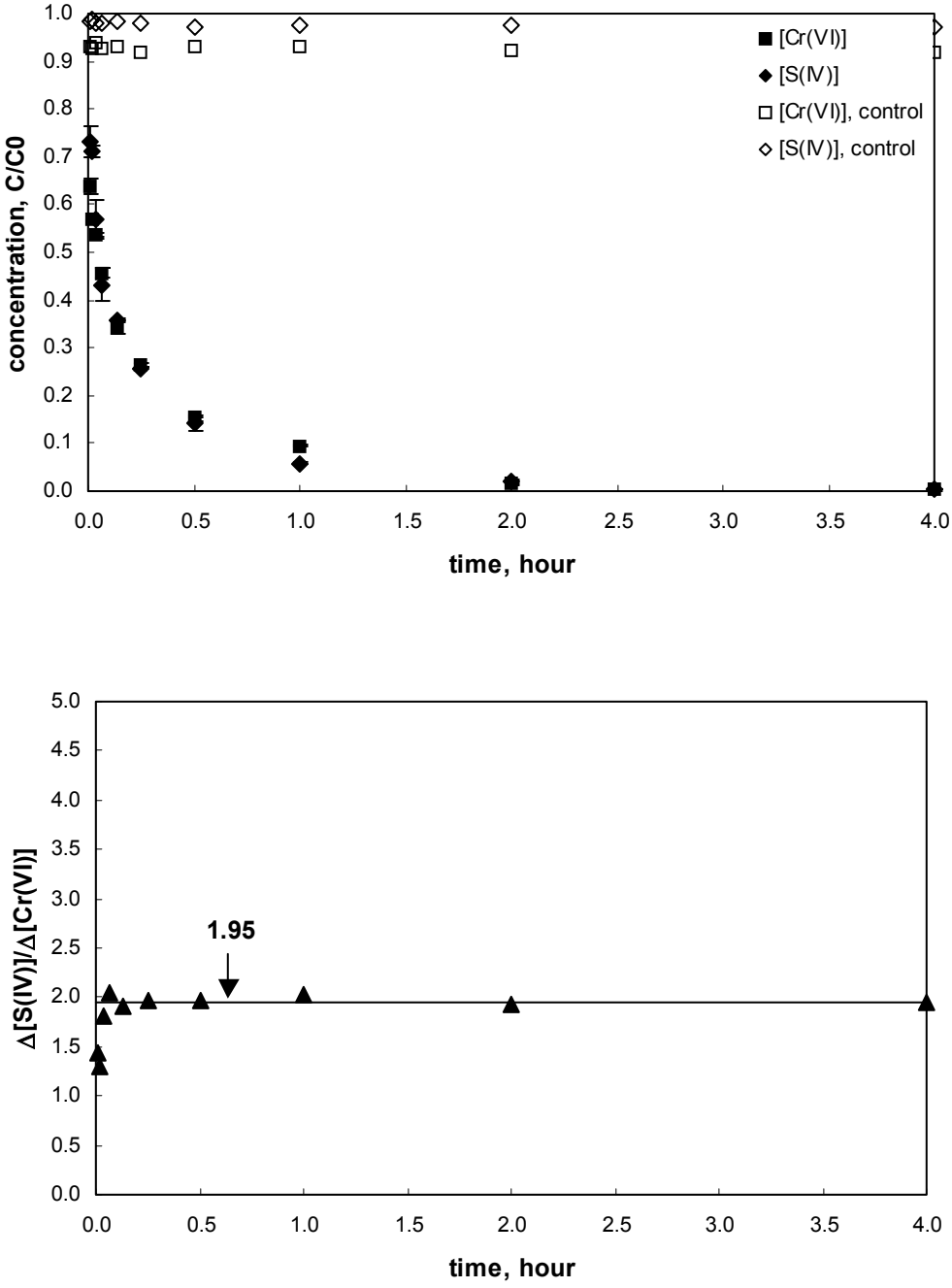

Figure 4-9. Stoichiometry of Cr(VI) reduction by sulfur dioxide (water content 0.25 g/g, initial concentrations [Cr(VI)] = 0.077 M & [S(IV)] = 0.15 M)

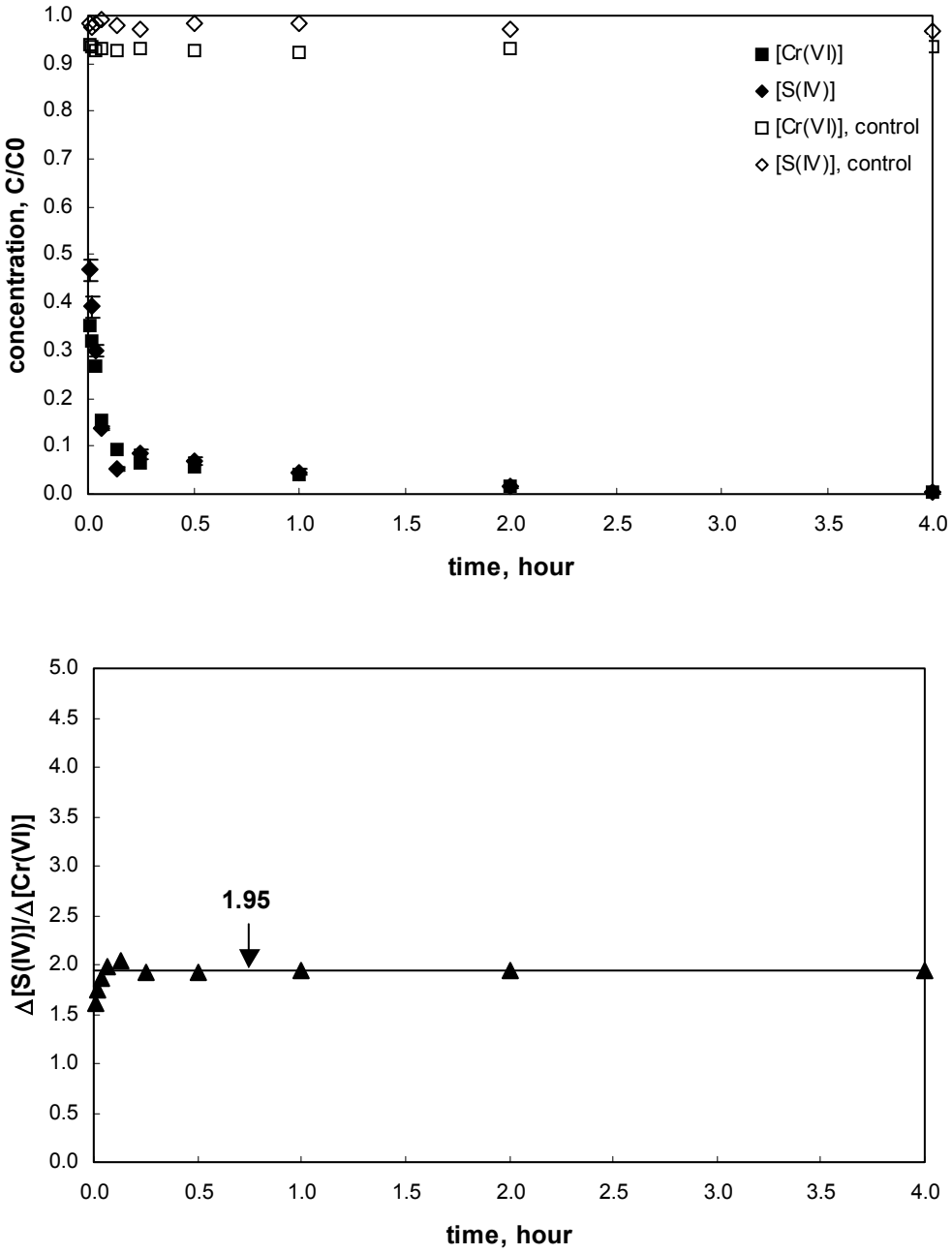

Figure 4-10. Stoichiometry of Cr(VI) reduction by sulfur dioxide (water content 0.05 g/g, initial concentrations [Cr(VI)] = 0.385 M & [S(IV)] = 0.75 M)

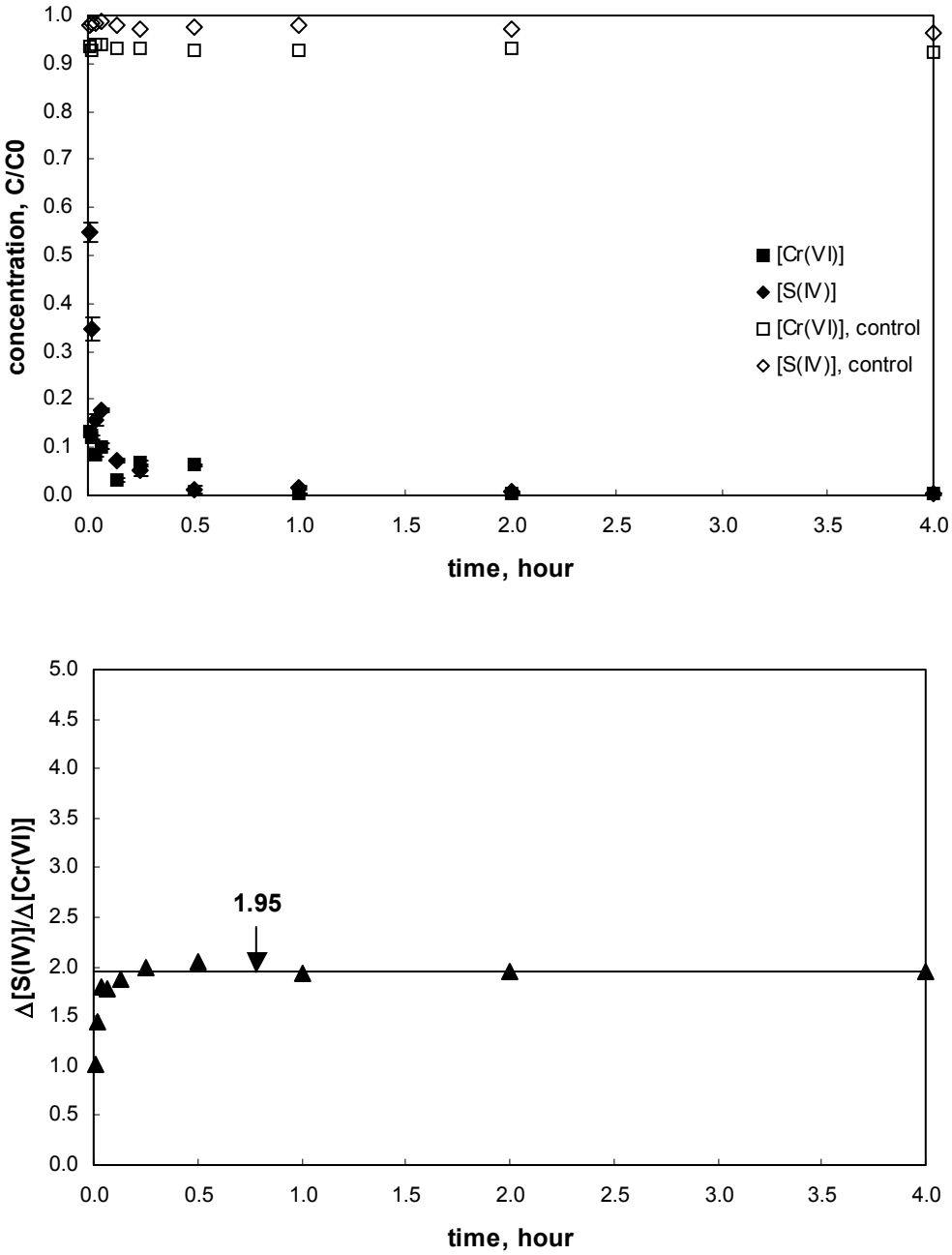

Figure 4-11. Stoichiometry of Cr(VI) reduction by sulfur dioxide (water content 0.01 g/g, initial concentrations [Cr(VI)] = 1.92 M & [S(IV)] = 3.75 M)

4.2.2. Kinetics of Cr(VI) reduction

Cr(VI) reduction in soil shows that the reaction is rapid, with a half-time less than 2 minutes, which is even faster than in water (half-time of about 45 minutes at pH 6 and about 16 hours at pH 7). The faster reaction in soil is due to the lower pH. The pH in the soil was 6.0 before reagents were added and 2.9 - 3.1 after the reaction was complete. The significant lowering of pH caused the reaction of Cr(VI) reduction to go faster.

The kinetic model developed in chapter (4.1.2.) and comprised of equations (4-3) and (4-4) was applied to describe Cr(VI) reduction in soil. Rate equations (4-5 through 4-7) were used for the calculation of kinetic parameters. The kinetic parameters, k_1 and k_2, were obtained by conducting nonlinear regressions on concentrations of Cr(VI), S(IV), and S(V) using MATLAB® (MathWorks Inc.). A range of reaction orders were assumed for these regressions and the best results were obtained when the reaction was assumed to be second-order with respect to [Cr(VI)] and first-order with respect to [S(IV)], and [S(V)]. The calculations showed relatively good fit to the data (figure 4-12), even though the fit looks worse than that for the data of aquatic kinetics. The calculated rate coefficients, k_1 and k_2, were 22 (± 41%) and 13 (± 77%) ($M^{-2}h^{-1}$).

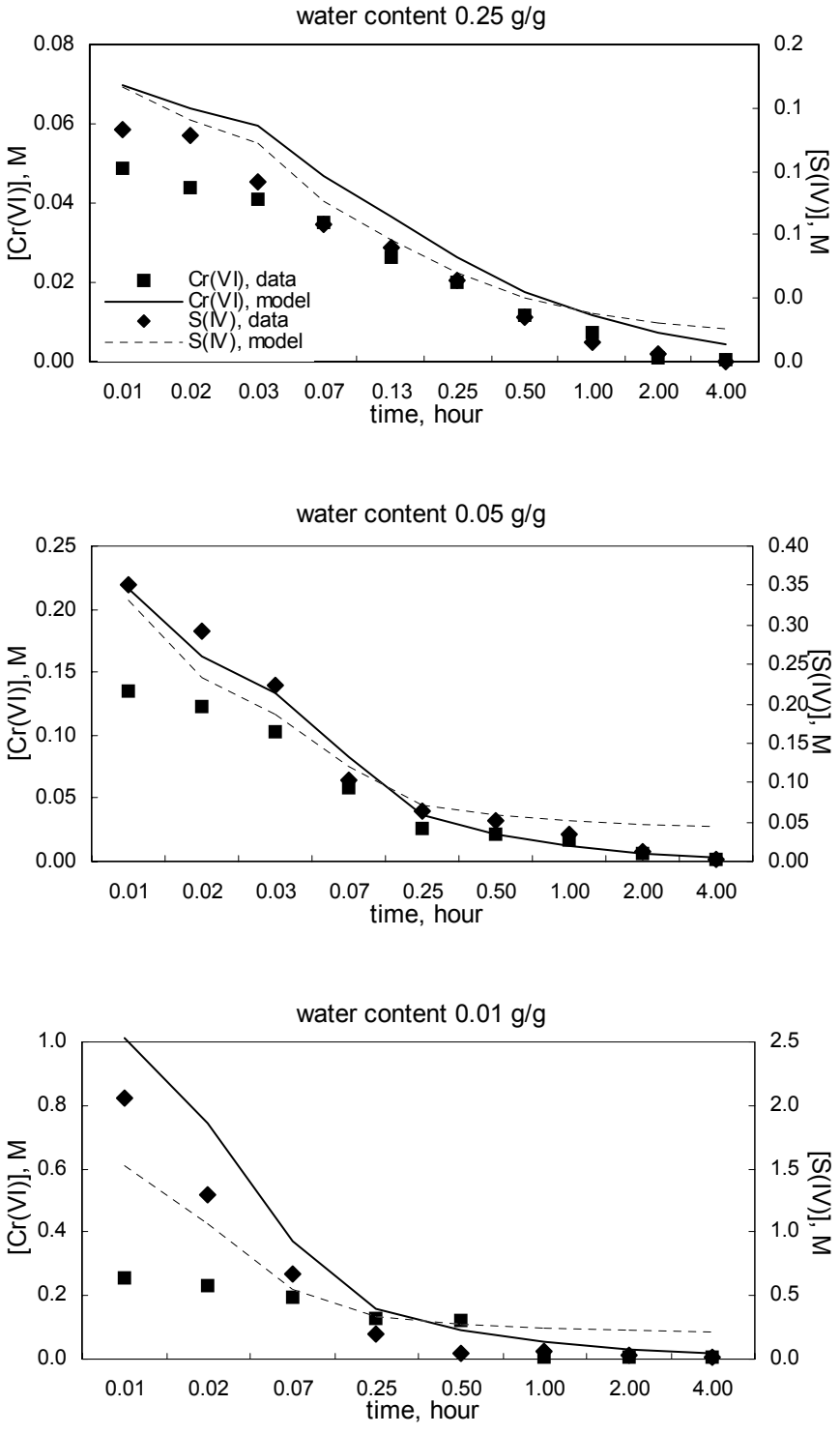

Figure 4-12. Kinetics of Cr(VI) reduction by sulfur dioxide in soil

4.2.3. The effect of water content

Water content does not affect the stoichiometry of Cr(VI) reduction by SO_2 in soil, but it does have some effect on the kinetics of the reaction. Overall, the reaction of Cr(VI) reduction proceeds with the similar kinetics and goes to an end within the same time period. But, in the early period of the reaction, the reaction is increasingly fast as water content decreases. This is possibly due to lower pH caused by lower water content.

CHAPTER V

SUMMARY AND CONCLUSIONS

Reduction of Cr(VI) to Cr(III) is an effective approach to remediation because it effectively reduces risk to human health and the environment through reduction in toxicity and mobility. Immobilization and detoxification of chromium in the vadose zone is made possible by the existence of an effective reductant, SO_2, that exists in a gaseous form at room temperature. Experimental studies were designed to characterize stoichiometry and kinetics of chromium reduction both in aqueous solution at pH values near neutrality and in soil.

First, batch experiments and elemental analyses were conducted to characterize stoichiometry and kinetics of Cr(VI) reduction in water. The effects of pH (pH 6, 7) and S(IV)/Cr(VI) ratio (0.5, 1.25, 5) were examined.

Experiments showed that the stoichiometric ratio of the change in S(IV) to the change in Cr(VI) ranged between 1.6 and 1.8, and that it is the result of a linear combination of two reactions (4-1 and 4-2) in which dithionate is an intermediate and sulfate is the stable oxidized product.

Experiments also showed that the reaction is rapid, with the half-time of about 45 minutes at pH 6 and about 16 hours at pH 7. A kinetic model was developed that assumed a two-step reaction, and included Cr(VI), S(IV), and S(V). The kinetic parameters were obtained by conducting nonlinear regression using MATLAB. The reaction was assumed to be second-order with respect to [Cr(VI)] and first-order with

respect to [S(IV)], and [S(V)]. The values for the rate coefficients for the first step (k_1) were 4.5 (± 10%), 0.25 (± 9.4%) ($mM^{-2}h^{-1}$) at pH 6 and 7, respectively. The values for the rate coefficient for the second step (k_2) were 25 (± 29%), 1.1 (± 30%) ($mM^{-2}h^{-1}$) for at pH 6 and 7, respectively.

Aqueous pH had some effect on the kinetics of the reaction. The reaction rate decreased as pH increased. Experiments showed that the rate at pH 7 was lower than at pH 6 by one order of magnitude. The stoichiometric ratio of S(IV) removed to Cr(VI) removed was in the range of 1.75 - 1.8 when the initial S(IV)/Cr(VI) ratio was 5, and 1.6 - 1.65 when the initial S(IV)/Cr(VI) ratio was 1.25 and 0.5.

Second, batch experiments were conducted to characterize stoichiometry and kinetics of Cr(VI) reduction in soil. The effect of water content (0.01, 0.05, 0.25 g/g) was investigated.

Experiments showed that the stoichiometry ratio of S(IV) removed to Cr(VI) removed was almost 2, which is higher than that for the reaction in water. This higher value may be caused by S(IV) oxidation by Fe(III) in soil minerals.

Cr(VI) reduction in soil is rapid, with the half-time less than 2 minutes, which is faster than in water. The faster reaction in soil was due to lower pH, which was near 3 after reaction was completed. The kinetics were modeled using a two-step reactions that included Cr(VI), S(IV), and S(V). The kinetic parameters were obtained by conducting nonlinear regression, using MATLAB. The reaction was assumed to be second-order with respect to [Cr(VI)] and first-order with respect to [S(IV)], and [S(V)]. The rate coefficients, k_1 and k_2, were 22 (± 41%) and 13 (± 77%) ($M^{-2}h^{-1}$).

Water content had some effects on the kinetics of the reaction. Overall, the reaction of Cr(VI) reduction proceeded with the similar kinetics and went to an end within the same time period. But, in the early period of the reaction, the reaction was increasingly fast as water content decreased. This is possibly due to decreasing pH caused from decreasing water content.

The first step of future research should be to focus on the ability of SO_2 to reduce redox-active components of the soil. This information will be useful in understanding the mechanism of Cr(VI) reduction in soils and in predicting the permanence of Cr(VI) reduction after SO_2 dissipates. The next step should be directed toward measuring the kinetics of SO_2 oxidation by oxygen. This data could be used to predict the fate of SO_2 in the vadose zone and aid design of remediation processes by determining whether extraction of SO_2 from the subsurface will be needed or whether it will naturally dissipate by in situ reaction with oxygen. In addition, the development of model for gas transport and reaction, and the test of model in soil columns should be conducted to predict effectiveness and cost of vadose zone remediation and to demonstrate reduction technology and test the model prediction.

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APPENDIX A

TABULATED DATA

Table A-1. Cr(VI) reduction by sulfur dioxide at pH 6 in water

S(IV)/Cr(VI) ratio 4.9				
time	Cr(VI)		S(IV)	
(hour)	C/C0*	stdev**	C/C0	stdev
0.1	0.92	4.49E-04	0.93	6.87E-03
0.3	0.80	4.72E-04	0.86	4.53E-03
0.5	0.65	1.75E-04	0.83	3.65E-03
0.8	0.51	2.87E-04	0.81	5.56E-03
1.0	0.43	5.55E-04	0.80	7.22E-03
1.5	0.34	4.86E-04	0.77	3.52E-03
2.0	0.29	5.61E-04	0.74	4.56E-03
3.5	0.20	4.54E-04	0.72	2.69E-03
6.0	0.15	5.15E-04	0.70	2.42E-03
12.0	0.05	5.43E-04	0.66	3.75E-03
24.0	0.01	5.89E-04	0.62	8.97E-03
48.0	0.00	4.98E-04	0.61	3.75E-03
72.0	0.00	1.86E-04	0.62	6.33E-03
S(IV)/Cr(VI) ratio 1.2				
time	Cr(VI)		S(IV)	
(hour)	C/C0	stdev	C/C0	stdev
0.3	0.95	7.54E-04	0.82	7.38E-03
0.5	0.93	7.62E-04	0.70	9.45E-03
1.0	0.84	9.57E-04	0.63	4.38E-03
1.5	0.78	1.25E-03	0.54	5.37E-03
2.0	0.74	7.57E-04	0.44	7.35E-03
3.0	0.66	5.60E-04	0.35	2.17E-03
6.0	0.55	1.59E-03	0.26	7.14E-03
12.0	0.47	5.63E-04	0.18	4.22E-03
24.0	0.34	5.63E-04	0.11	8.51E-04
48.0	0.24	5.40E-04	0.00	2.54E-03
72.0	0.25	5.79E-04	0.00	5.43E-03
120.0	0.24	5.56E-04	0.00	3.73E-03
S(IV)/Cr(VI) ratio 0.49				
time	Cr(VI)		S(IV)	
(hour)	C/C0	stdev	C/C0	stdev

0.3	0.98	1.24E-03	0.79	8.43E-03
0.5	0.93	9.32E-04	0.66	3.21E-03
1.0	0.91	3.49E-04	0.53	2.12E-03
1.5	0.89	5.36E-04	0.46	3.89E-03
2.0	0.87	8.82E-04	0.41	3.66E-03
3.0	0.84	1.07E-03	0.33	2.58E-03
6.0	0.77	1.28E-03	0.23	2.99E-04
12.0	0.73	5.24E-04	0.12	3.21E-03
24.0	0.69	1.06E-03	0.00	4.20E-03
48.0	0.69	7.32E-04	0.00	2.45E-03
72.0	0.69	5.97E-04	0.00	6.86E-04

*C/C0: relative concentration, **stdev: standard deviation

Table A-2. Cr(VI) reduction by sulfur dioxide at pH 7 in water

S(IV)/Cr(VI) ratio 4.9				
time	Cr(VI)		S(IV)	
(day)	C/C0	stdev	C/C0	stdev
0.1	0.90	9.11E-04	0.91	1.37E-02
0.2	0.79	3.16E-03	0.88	7.51E-03
0.3	0.71	4.11E-03	0.86	4.05E-03
0.4	0.62	1.41E-03	0.83	5.28E-03
0.7	0.48	5.49E-04	0.78	3.63E-03
1.1	0.40	1.93E-03	0.75	7.37E-03
1.8	0.28	9.27E-04	0.71	3.17E-03
3.0	0.18	3.91E-04	0.67	1.45E-02
5.1	0.12	7.49E-04	0.65	1.30E-03
8.7	0.07	1.02E-03	0.65	5.36E-03
15.8	0.02	9.54E-04	0.65	5.74E-03
22.6	0.04	9.99E-04	0.66	3.75E-03
32.0	0.03	7.85E-04	0.65	6.33E-03
S(IV)/Cr(VI) ratio 1.2				
time	Cr(VI)		S(IV)	
(day)	C/C0	stdev	C/C0	stdev
0.1	0.98	3.38E-03	0.93	1.51E-03
0.3	0.92	1.15E-03	0.87	2.71E-03
0.9	0.82	2.04E-03	0.71	1.62E-03
1.4	0.74	1.33E-03	0.65	9.97E-04
2.4	0.60	1.10E-03	0.49	4.78E-03
4.1	0.45	1.09E-03	0.24	5.03E-03
8.3	0.28	2.49E-03	0.12	4.09E-03
16.3	0.23	3.41E-03	0.03	1.11E-03
32.2	0.22	2.63E-03	0.00	3.51E-03

40.0	0.22	1.40E-03	0.00	1.54E-03
67.9	0.23	1.79E-03	0.00	1.95E-03
S(IV)/Cr(VI) ratio 0.49				
time	Cr(VI)		S(IV)	
(day)	C/C0	stdev	C/C0	stdev
0.4	0.98	5.13E-03	0.85	2.49E-03
1.2	0.94	1.32E-03	0.73	9.75E-04
2.1	0.90	2.41E-03	0.63	3.62E-03
3.1	0.86	3.30E-03	0.50	4.84E-03
4.1	0.83	3.10E-03	0.36	4.84E-03
8.2	0.76	1.27E-03	0.15	3.66E-03
15.2	0.71	1.71E-03	0.03	2.58E-03
29.2	0.70	1.71E-03	0.00	2.99E-03
37.1	0.70	2.52E-03	0.00	3.21E-03
64.9	0.70	3.32E-03	0.00	2.45E-03

Table A-3. Cr(VI) reduction by sulfur dioxide in soil

water content 0.25 g/g				
time	Cr(VI)		S(IV)	
(hour)	C/C0	stdev	C/C0	stdev
0.01	0.637	0.016	0.731	0.033
0.02	0.569	0.002	0.711	0.013
0.03	0.535	0.004	0.570	0.041
0.07	0.457	0.010	0.432	0.034
0.13	0.343	0.015	0.357	0.003
0.25	0.263	0.004	0.258	0.001
0.50	0.153	0.005	0.142	0.014
1.00	0.095	0.002	0.058	0.003
2.00	0.015	0.001	0.022	0.001
4.00	0.004	0.001	0.003	0.001
water content 0.05 g/g				
time	Cr(VI)		S(IV)	
(hour)	C/C0	stdev	C/C0	stdev
0.01	0.351	0.010	0.468	0.021
0.02	0.318	0.002	0.391	0.023
0.03	0.267	0.006	0.299	0.013
0.07	0.153	0.003	0.139	0.004
0.13	0.094	0.004	0.054	0.004
0.25	0.066	0.005	0.084	0.010
0.50	0.055	0.004	0.068	0.008
1.00	0.042	0.002	0.046	0.005
2.00	0.015	0.001	0.015	0.002

4.00	0.003	0.001	0.003	0.001
water content 0.01 g/g				
time	Cr(VI)		S(IV)	
(hour)	C/C0	stdev	C/C0	stdev
0.01	0.351	0.010	0.01	0.351
0.02	0.318	0.002	0.02	0.318
0.03	0.267	0.006	0.03	0.267
0.07	0.153	0.003	0.07	0.153
0.13	0.094	0.004	0.13	0.094
0.25	0.066	0.005	0.25	0.066
0.50	0.055	0.004	0.50	0.055
1.00	0.042	0.002	1.00	0.042
2.00	0.015	0.001	2.00	0.015
4.00	0.003	0.001	4.00	0.003

APPENDIX B

SOURCE FILES (M-FILES) FOR COMPUTER PROGRAM (MATLAB®) TO CALCULATE KINETIC PARAMETERS FOR THE KINETICS OF CHROMIUM(VI) REDUCTION BY SULFUR DIOXIDE

% This example is for the calculation of data at pH 6.

runnlinfit6.m

```
function  [beta,betaci,t,cmeas] = runnlinfit6(dataname,beta0)
% function that calls other functions to conduct non-linear least squares regression on
% data points in 'dataname' using initial estimates of parameters.

data1 = load('data6a.txt');  % data file for pH 6 & S/Cr ratio 5
t1 = data1(:,1);       % measured values of time
t1 = [t1;t1+100];
cmeas1 = [data1(:,2);data1(:,3)]; % measured values of Cr(VI) & S(IV)

data2 = load('data6b.txt');  % data file for pH 6 & S/Cr ratio 1.25
t2 = data2(:,1);
t2 = [t2+200;t2+300];
cmeas2 = [data2(:,2);data2(:,3)];

data3 = load('data6c.txt');  % data file for pH 6 & S/Cr ratio 0.5
t3 = data3(:,1);
t3 = [t3+400;t3+500];
cmeas3 = [data3(:,2);data3(:,3)];

t = [t1;t2;t3];
cmeas = [cmeas1;cmeas2;cmeas3];
beta0 = [1 1];  % initial estimates of kinetic parameters
[beta,resid,j] = nlinfit(t,cmeas,@calcc6,beta0);
% call function to do least-sqares regression
betaci = nlparci(beta,resid,j);
% call function to calculate confidence intervals
beta
betaci
```

calcc6.m

```
function  cmod=calcc6(beta,t)
% function to calculate concentrations at time t from model

data1 = load('data6a.txt');
t1 = data1(:,1);
t1 = [0;t1]; % add point at t=0
c10 = [0.1923 0.9387 0]; % initial concentration of Cr(VI),S(IV) & S(V)
options = [];
[tmod1,cmod1] = ode45(@rateeqn61,t1,c10,options,beta);
cmod1 = [cmod1(2:end,1);cmod1(2:end,2)];
% remove initial concentration, i.e. point at t=0

% calculation of sum of squared errors(SS)
% the iteration number is equal to that of rows of data file
%----------
cmeas1 = [data1(:,2);data1(:,3)];
SS1 = 0;
for i=1:13
   SSE_Cr1 = ((cmeas1(i)-cmod1(i))/0.1923)^2;
   SS1 = SS1 + SSE_Cr1;
end
for i=14:26
   SSE_S1 = ((cmeas1(i)-cmod1(i))/0.9387)^2;
   SS1 = SS1 + SSE_S1;
end
SS1;
%----------

data2 = load('data6b.txt');
t2 = data2(:,1);
t2 = [0;t2];
c20 = [0.1923 0.2346 0];
options = [];
[tmod2,cmod2] = ode45(@rateeqn62,t2,c20,options,beta);
cmod2 = [cmod2(2:end,1);cmod2(2:end,2)];
%----------
cmeas2 = [data2(:,2);data2(:,3)];
SS2 = 0;
for i=1:10
   SSE_Cr2 = ((cmeas2(i)-cmod2(i))/0.1923)^2;
   SS2 = SS2 + SSE_Cr2;
```

```
end
for i=11:20
   SSE_S2 = ((cmeas2(i)-cmod2(i))/0.2346)^2;
   SS2 = SS2 + SSE_S2;
end
SS2;
%----------

data3 = load('data6c.txt');
t3 = data3(:,1);
t3 = [0;t3];
c30 = [0.1923 0.09387 0];
options = [];
[tmod3,cmod3] = ode45(@rateeqn63,t3,c30,options,beta);
cmod3 = [cmod3(2:end,1);cmod3(2:end,2)];
%----------
cmeas3 = [data3(:,2);data3(:,3)];
SS3 = 0;
for i=1:10
   SSE_Cr3 = ((cmeas3(i)-cmod3(i))/0.1923)^2;
   SS3 = SS3 + SSE_Cr3;
end
for i=11:20
   SSE_S3 = ((cmeas3(i)-cmod3(i))/0.09387)^2;
   SS3 = SS3 + SSE_S3;
end
SS3;
%----------

cmod = [cmod1;cmod2;cmod3]
SS = SS1 + SS2 + SS3
```

rateeqn61.m

```
function  dc1 = rateeqn61(t1,c1,beta)
% function to calculate derivative of concentration with respect to time using batch
% material balance and rate equation

% 2 reactions are considered:
% Cr(VI) + 3S(IV) -> Cr(III) + 3S(V) with rate constant, k1
% Cr(VI) + 3S(V) -> Cr(III) + 3S(VI) with rate constant, k2
%
% 2 rate equations are built:
```

```
% r1 = k1 x [Cr(VI)]^a1 x [S(IV)]^b1
% r2 = k2 x [Cr(VI)]^a2 x [S(V)]^b2
%
% d[Cr(VI)]/dt = -r1 – r2; d[S(IV)]/dt = -3r1; d[S(V)]/dt = 3r1 – 3r2


a1=2;a2=2;b1=1;b2=1;

k1 = beta(1);
k2 = beta(2);

dc1 = zeros(3,1);
dc1(1) = -k1*c1(1)^a1*c1(2)^b1 - k2*c1(1)^a2*c1(3)^b2;
dc1(2) = -3*k1*c1(1)^a1*c1(2)^b1;
dc1(3) = 3*k1*c1(1)^a1*c1(2)^b1 - 3*k2*c1(1)^a2*c1(3)^b2;
```

rateeqn62.m

```
function  dc2 = rateeqn62(t2,c2,beta)
% function to calculate derivative of concentration with respect to time using batch
% material balance and rate equation

a1=2;a2=2;b1=1;b2=1;

k1 = beta(1);
k2 = beta(2);

dc2 = zeros(3,1);
dc2(1) = -k1*c2(1)^a1*c2(2)^b1 - k2*c2(1)^a2*c2(3)^b2;
dc2(2) = -3*k1*c2(1)^a1*c2(2)^b1;
dc2(3) = 3*k1*c2(1)^a1*c2(2)^b1 - 3*k2*c2(1)^a2*c2(3)^b2;
```

rateeqn63.m

```
function  dc3 = rateeqn63(t3,c3,beta)
% function to calculate derivative of concentration with respect to time using batch
% material balance and rate equation

a1=2;a2=2;b1=1;b2=1;

k1 = beta(1);
k2 = beta(2);
```

```
dc3 = zeros(3,1);
dc3(1) = -k1*c3(1)^a1*c3(2)^b1 - k2*c3(1)^a2*c3(3)^b2;
dc3(2) = -3*k1*c3(1)^a1*c3(2)^b1;
dc3(3) = 3*k1*c3(1)^a1*c3(2)^b1 - 3*k2*c3(1)^a2*c3(3)^b2;
```

data files

data6a.txt		
time, hour	[Cr(VI)], mM	[S(IV)], mM
0.08	1.78E-01	8.75E-01
0.25	1.55E-01	8.06E-01
0.50	1.25E-01	7.82E-01
0.75	9.74E-02	7.56E-01
1.00	8.25E-02	7.52E-01
1.50	6.52E-02	7.25E-01
2.00	5.58E-02	6.99E-01
3.50	3.78E-02	6.77E-01
6.00	2.90E-02	6.60E-01
12.0	9.11E-03	6.22E-01
24.0	1.41E-03	5.78E-01
48.0	4.00E-04	5.72E-01
72.0	4.00E-04	5.72E-01
data6b.txt		
time, hour	[Cr(VI)], mM	[S(IV)], mM
0.50	1.80E-01	1.64E-01
1.00	1.62E-01	1.47E-01
1.50	1.51E-01	1.27E-01
2.00	1.42E-01	1.03E-01
3.00	1.28E-01	8.22E-02
6.00	1.06E-01	6.02E-02
12.0	9.03E-02	4.21E-02
24.0	6.61E-02	2.54E-02
48.0	4.66E-02	1.64E-03
72.0	4.66E-02	1.64E-03
data6c.txt		
time, hour	[Cr(VI)], mM	[S(IV)], mM
0.25	1.88E-01	7.44E-02

0.50	1.79E-01	6.17E-02
1.00	1.74E-01	5.00E-02
1.50	1.71E-01	4.35E-02
2.00	1.67E-01	3.82E-02
3.00	1.61E-01	3.08E-02
6.00	1.48E-01	2.21E-02
12.0	1.40E-01	1.15E-02
24.0	1.32E-01	7.44E-04
48.0	1.32E-01	7.44E-04

VITA

Min Ahn was born in Seoul, Korea. He grew up in Seoul, Korea. He received a Bachelor of Science degree in geology at Seoul National University in 1991. He started his master's program at Texas A&M University in 1998. His research was been focused on remediation of soils contaminated with hexavalent chromium that are reduced by reductants, such as sulfur dioxide, and immobilized. His research interest includes stoichiometry and kinetics of Cr(VI) reduction by sulfur dioxide. His permanent address is 35/2 176-37 Sadang-Dong, Seoul, Korea, 156-093.